PB82-125014

Nitrosamines in Vehicle Interiors

Southwest Research Inst.
San Antonio, TX

Prepared for

Environmental Protection Agency
Ann Arbor, MI

Sep 81

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Office of Mobile Source Air Pollution Control
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, Michigan 48105

EPA-460/3-81-029
September 1981

PB82-125014

Air

EPA

Nitrosamines In Vehicle Interiors

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NATIONAL TECHNICAL
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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-460/3-81-029		PB82 125014

4. TITLE AND SUBTITLE
NITROSAMINES IN VEHICLE INTERIORS

5. REPORT DATE
September 1981

6. PERFORMING ORGANIZATION CODE
U306001

7. AUTHOR(S)
Lawrence R. Smith

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Southwest Research Institute
6220 Culebra Road
San Antonio, Texas 78284

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-03-2884

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Protection Agency
Mobile Source Air Pollution Control
2565 Plymouth Road
Ann Arbor, Michigan 48105

13. TYPE OF REPORT AND PERIOD COVERED
Final-June 1980-May 1981

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Motor Vehicle Nitrosamines	Nitrosamine Analysis Nitrosamine Collection Occupant Exposure Vehicle Interiors	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release Unlimited	Unclassified	70
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

EPA-460/3-81-029

Nitrosamines In Vehicle Interiors

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Contract No. 68-03-2884
Task Specification 2

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Office of Mobile Source Air Pollution Control
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2565 Plymouth Road
Ann Arbor, Michigan 48105

September 1981

1-a

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Publication No. EPA-460/3-81-029

FOREWORD

This project was conducted for the U. S. Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan 48105, by the Department of Emissions Research of Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas 78284. Nitrosamine analyses in the project were conducted by the New England Institute for Life Sciences, 125 Second Avenue, Waltham, Massachusetts 02154. This project, authorized by Contract 68-03-2884, Task 2, was initiated on June 5, 1980 and completed May 5, 1981. The EPA Project Officer was Mr. Robert J. Garbe and the EPA Task Technical Officer was Mr. Thomas M. Baines, both of the Emission Control Technology Division, Environmental Protection Agency. Ms. Laurie Gallagher of the ECTD, EPA provided major assistance in vehicle acquisition and sample collection in Ann Arbor, Michigan. Dr. David Fine of the New England Institute for Life Sciences was in charge of the sample analyses for the project. The SwRI Project Leader and principal researcher for the project was Dr. Lawrence R. Smith. The SwRI Task Technical Supervisor was Harry E. Dietzmann, and the SwRI Project Manager was Charles T. Hare. Key technical personnel involved at SwRI included D. R. Terrazas and J. C. Chessher. This project was identified within Southwest Research Institute as Project No. 11-5830-002.

ABSTRACT

Researchers in the nitrosamine field were contacted on their views of the TEA analyzer and ThermoSorb/N Air Samplers for nitrosamine analysis. Gas samples were taken from vehicle interiors to determine the effects of vehicle type, vehicle age, mode of operation, and ambient conditions on interior nitrosamine levels. A total of fifty-eight vehicles were sampled in the program. Occupant exposure levels were estimated using test vehicle data.

SUMMARY

The objectives of this project were to determine whether or not a nitrosamine analytical procedure which has the consensus backing of the scientific community exists, and then to provide gas samples from vehicle interiors to be analyzed for nitrosamines. Various test vehicles and test sequences were selected to determine influences of vehicle type, vehicle age, mode of operation, and ambient conditions on interior nitrosamine levels and to determine occupant exposure levels.

The response from the scientific community for the most part indicated an acceptance of the TEA analyzer and ThermoSorb/N traps. Researchers using both the TEA analyzer and ThermoSorb/N traps felt that both are the best available for routine analysis work.

Of the fifty-six vehicles sampled in the program by SwRI, detectable levels of nitrosamines were found in forty-seven. Concentrations of detectable nitrosamines in vehicle interiors ranged from 0.01 to 0.63 $\mu g/m^3$. N-nitrosodimethylamine (NDMA) was found in all forty-seven vehicles with detectable levels of NDMA at concentrations ranging from 0.01 to 0.39 $\mu g/m^3$. N-nitrosodiethylamine (NDEA), N-nitrosomorpholine (NMOR), N-nitrosodipropylamine (NDPA), and N-nitrosodibutylamine (NDBA) were found in 12 or fewer vehicles at levels ranging from 0.01 to 0.16 $\mu g/m^3$. Both NDMA (ND-0.24 $\mu g/m^3$) and NMOR (ND-0.360 $\mu g/m^3$) were found in two vehicles sampled by the New England Institute for Life Sciences.

Test results indicated NDMA dependence on mileage and time, with NDMA levels decreasing slightly with time and mileage; NDMA dependence on temperature, with higher temperatures giving higher levels of NDMA; the presence of detectable levels of NDMA in vehicles during operation; and similar levels of NDMA in vehicles closed overnight versus vehicles closed for only a short time. Nitrosamines were found in passenger cars, station-wagons, passenger and cargo vans, pickup trucks, and in new and used heavy-duty trucks. Nitrosamines were not detected in motor homes. On the average, the daily intake of nitrosamines from vehicle interiors is estimated to be less than that from a can of beer or from a strip of bacon.

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I. INTRODUCTION

The presence of nitrosamines in car interiors was first determined by the New England Institute for Life Sciences. Nitrosamines were found in 37 of 38 new 1979 cars at concentrations ranging from 0.07 to 2.9 $\mu g/m^3$.(1,2)* The estimated exposure to man was reported to be similar to that from bacon and beer. This report describes an effort to further assess the magnitude and scope of the problem of nitrosamines in all types of vehicle interiors, as well as evaluate some of the variables influencing nitrosamine levels.

A. Project Objectives

The objectives of this project were to determine whether or not a nitrosamine analytical procedure which has the consensus backing of the scientific community exists, and then provide samples from a variety of vehicle interiors to be analyzed for nitrosamines. A variety of vehicles and test situations were selected to determine influences of vehicle age, mode of operation, and ambient conditions on interior nitrosamine concentrations. Occupant exposures were to be estimated using the resulting data.

B. Approach and Scope

To effectively accomplish the project objectives, the project was carried out in six tasks. The first task consisted of a peer review of the sampling and analytical methodology used by the New England Institute for Life Sciences (NEILS) to determine nitrosamine levels in car interiors. If this methodology was found acceptable to the scientific community, it would be used in the program for sample collection and analysis. Due to the relatively brief duration of the project and the relatively long set-up time needed for the method, samples were to be analyzed by NEILS if the methodology was found acceptable.

Also, during each of the following tasks, several samples were taken to determine: 1) level of nitrosation potential of the air, 2) level of nitrosatable amines in the air, and 3) level of nitrosamines in ambient air. These samples were collected using methodology developed at NEILS. After collection at SwRI, samples were sent to NEILS for analysis. Additional nitrosation potential information was obtained by monitoring the NO_x levels in selected circumstances with a TECO chemiluminescent NO_x analyzer. Additional nitrosatable amine information was obtained

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*Numbers in parentheses designate references at end of report.

by collecting selected organic amines sampled in dilute sulfuric acid, and analyzing the samples with a gas chromatograph (GC) equipped with a nitrogen phosphorus detector (NPD) and an ascarite precolumn.

In the second task, four vehicles (two at Southwest Research Institute and two at NEILS) were monitored once a month over a six month period to determine the effects of time on interior nitrosamine levels. Mileage was also recorded as an additional variable at SwRI. To determine the influence of operation, twelve vehicles were sampled before, during and after operation in the third task. One vehicle was sampled: 1) immediately before operation, 2) at four sequential times during operation, traps sampled at 0, 1, 5, and 10 minutes into the trip, and 3) immediately after the trip. In the fourth task, EPA assisted SwRI by obtaining 15 new vehicles in Ann Arbor. These vehicles were sampled at ambient temperature at the EPA-Ann Arbor lab by SwRI. Nine of the vehicles with the highest nitrosamine levels were selected for additional testing, and were sampled at 40° and 100°F in EPA's cold room. Twenty-five vehicles were sampled in the fifth task as an additional assessment to increase the data base for interior nitrosamine concentrations. Vehicles sampled in this task included motor homes, new and used heavy-duty trucks, new vans, pickup trucks, and station wagons. In the sixth task, an exposure assessment was carried out for several population categories using the data generated in the previous tasks. The following situations were investigated: 1) continuous exposure, 2) worst case commuter exposure, and 3) typical case commuter exposure.

II. GENERAL EQUIPMENT AND TEST PROCEDURES

This section contains a description of the test equipment and procedures used to collect the nitrosamine samples as well as a brief review of the analytical procedures used by NEILS to analyze for nitrosamine, nitrosation potential and nitrosatable amines.

A. ThermoSorb/N Air Sampler

All nitrosamine samples were collected using ThermoSorb/N Air Samplers which were developed by the Thermo Electron Corporation. The air sampler cartridge is shown in Figure 1.

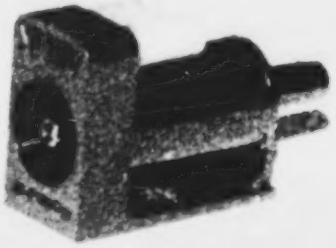

Figure 1. ThermoSorb/N air sampler.

The ThermoSorb/N Air Sampler cartridge has been reported in the literature to be free of artifact formation and capable of retaining 100% of preloaded nitrosamines.(3)

The air sample is pulled through the cartridge with the use of a battery operated sample pump. The cartridges contain a solid sorbent of metal silicates, which have been activated in a reducing atmosphere, for the collection of nitrosamines; as well as a nitrosation inhibitor and an amine trap to prevent artifact formation in the cartridge. The cartridges are constructed of medical-grade polyethylene with 100 mesh stainless steel screens at the inlet and outlet, and with standard Luer fittings to facilitate solvent elution

of the trapped nitrosamines. During testing, flow rates of 2 to 4 liters/minute were used to collect the samples. The cartridges are reported to efficiently collect nitrosamines at these flow rates. The cartridges were used and handled as directed by Thermo Electron in their "Instructions for Monitoring" (Appendix A).

B. Sample Pumps

The sample pumps used in this program were DuPont Constant Flow Samplers (Models P-2500 and P-4000). These pumps are battery powered, and are capable of moving a constant volume flow rate of air through a collection device. Both models possess an automatic flow control system which maintains a constant air flow rate within ±5% over pressure drop changes up to 15 inches of water column. These automatic flow control systems are necessary when sampling the interior of a vehicle for several hours with all windows and doors closed. The P-2500 has a sampling range of 1000 to 25000 cc/min and the P-4000 has a sampling range of 500 to 4000 cc/min. Both can operate for eight hours before recharging. Figure 2 shows the P-2500 and the P-4000 sample pumps connected to ThermoSorb/N Air Samplers. The pumps were calibrated before and after testing with a ThermoSorb/N Air Sampler attached. A stopwatch and a bubble tower were used to determine the air flow.

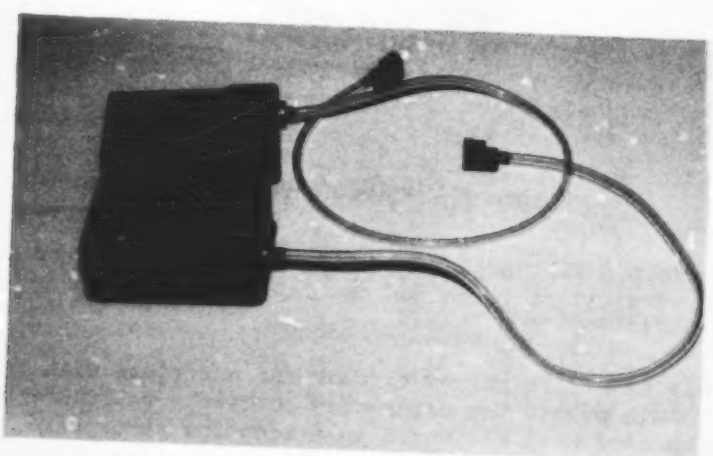

Figure 2. P-2500 and P-4000 sample pumps connected to ThermoSorb/N Air Samplers

C. Nitrosamine Analysis: GC-TEA

When received at NEILS, the ThermoSorb/N Air Samplers were immediately backflushed with a 25/75 solution of methanol in dichloromethane at a rate of 0.5 mℓ/min. The first 1.5 to 1.8 mℓ of this eluate was saved for chromatographic analysis. This elution step has been previously described in the literature.(3)

Two analyzers were used at NEILS for the GC-TEA analysis of the nitrosamine samples. The first GC-TEA analyzer system consisted of a Shimadzu Mini 2 GC with a temperature programmer interfaced to a TEA analyzer (Model 502). The TEA signal was recorded using a Hewlett-Packard intergrating recorder (Model 3308A). The GC column consisted of a 14' x 1/8" stainless steel column packed with 10% Carbowax 20M containing 0.5% KOH on Chromosorb HP (80-100 mesh). The column was operated at 150°C for isothermal separations, or programmed at 6°/min from 130° to 200°C. Argon gas (flow rate 15 mℓ/min) was used as the carrier gas. The TEA analyzer was operated with a specially designed sorbent dry trap instead of the usual cryogenic. For maximum sensitivity 15 µℓ of each sample was injected into the GC rather than the usual 4-5 µℓ. The second analysis of the Task II samples were analyzed with this system.

The second GC-TEA analyzer system used for nitrosamine analysis at NEILS consisted of a Hewlett-Packard Model 5710A with a Model 7671 Autosampler interfaced to a TEA Model 543 analyzer. The TEA signal was recorded using a Spectra-Physics 4060 Printer Plotter/SP4000 CPU system. The GC column consisted of a 1/4" x 6' glass column packed with 10% Carbowax 20M containing 0.5% KOH on Chromosorb WHP (80-100 mesh). The column was operated with a temperature program from 140°C to 170°C at 4°C per minute. Argon was the carrier gas with a flow rate of 20 mℓ/min. Sample injection volumes ranged from 4.5 to 10 µℓ.

D. Confirmational LC-TEA Analysis

The LC-TEA system used to confirm the GC-TEA analyses consisted of a Waters 6000A solvent delivery system with a U6K Universal injector interfaced to a TEA Model 502 Analyzer operating in the HPLC mode. The signal was recorded using a Soltec dual-pen recorder. The column used was a 10 µm Lichosorb Si 60 (4.6 x 250 mm). The mobile phase was 7% acetone in isooctane, and a flow rate of 2.0 cc per minute was maintained.

E. Confirmational Mass Spectral Analysis

To confirm the GC- and LC-TEA analyses, gas chromatography-high resolution mass spectral analyses (GC-MS) were performed. Due to the small quantities of nitrosamines collected in individual ThermoSorb air samplers, it was necessary to combine several samples in order to obtain sufficient quantities of nitrosamines for mass spectral analyses. Three composite samples were obtained in this manner.

The composite samples were diluted ten-fold with distilled water and extracted three times with dichloromethane (DCM). The DCM extracts were dried over anhydrous sodium sulfate and concentrated to one milliliter using a Kuderna-Danish evaporator at 54°C. The concentrated extracts were re-examined by GC-TEA before mass spectral analysis.

The GC-MS system used to analyze the composite samples consisted of a glass capillary column connected directly to the ion source of the mass spectrometer. The glass capillary column was 20 m x 0.25 mm I.D. and coated with Carbowax 20M. The mass spectrometer was an AEI MS50 instrument operated at a resolution of 10,000 (10% valley). A detailed description of the mass spectrometer can be found in Appendix B.

F. Collection and Analysis Procedure for Determining Nitrosation Capacity

The nitrosation potential of the ambient air was determined in the program by the use of sample cartridges similar to the ThermoSorb/N air samplers used for nitrosamine collection. The cartridges were filled with a solid sorbent coated with morpholine. Air samples were pulled through the cartridges at a flow rate of 1 liter per minute for 50 minutes. Any NO_2 present in the air sample reacts with the morpholine in the cartridge to produce N-nitrosomorpholine. The amount of N-nitrosomorpholine present in the cartridge has been found by NEILS to be proportional to the concentration of NO_2 in the sampled air. The analysis of the N-nitrosomorpholine in the cartridges was conducted by GC-TEA as if it were from a ThermoSorb/N air sampler. A more detailed description of the nitrosation capacity determination can be found in Appendix C. This description of the analysis procedure was provided by NEILS to SwRI with sample analyses.

G. Analysis of Air Samples for Amines

The amine air samples were collected using ThermoSorb/Amine Air Cartridges. The methods for collection and analysis of amines were similar to those used for nitrosamines on ThermoSorb/N air cartridges. After sample collection, the cartridges were backflushed with water, with the first milliliter collected for analysis. Aliquots of this eluate were then analyzed by injecting into a gas chromatograph interfaced to a prototype TEA Analyzer operating in the nitrogen mode. The analyzer used for the study was a Varian 3700 GC operating from 60 to 220°C at 10° C/min, with a hold at 60°C for 1 minute, interfaced to a catalytic oxidative pyrolytic furnace. A 2 mm I.D. x 6' glass column packed with Carbopak B was used for the GC separation. Argon was the carrier gas with a flow rate of 20 cc/min. Detection of the NO radical formed from the high temperature oxidation of the amines was by a standard TEA analyzer. A more detailed description of this system can be found in Appendix D. This description of the procedure was provided by NEILS to SwRI with sample results.

A minimum number of amine samples were collected and anayzed at SwRI. These samples were collected by bubbling air samples through glass impingers containing 0.01 N sulfuric acid, and analyzing a portion of the collecting solution with the aid of a gas chromatograph equipped with an ascarite-loaded pre-column and a nitrogen-phosphorus detector (NPD). A complete description of this procedure is available in the literature.(4)

H. Test Sequence to Determine Influence of Vehicle Age at SwRI - Task II

The vehicles tested in the SwRI portion of this task were employee-owned, and were tested during SwRI working hours (8:00 AM to 5:00 PM). Four vehicles were sampled in an initial screening process, and two of these four vehicles were sampled once a month over a six month time period. A description of the vehicles tested in this task can be found in Section III-B of this report. All vehicles were tested in this task using the following sequence:

1. Vehicle driven into the Emissions Lab (8:00 AM to 8:30 AM)

2. Vehicle allowed to stand for 2 to 2 1/2 hours with the hood raised and the windows open. Fan used to blow air across engine during this period.

3. Interior air blown out with a fan to remove all traces of nitrosamines that could have previously accumulated.

4. Hood, windows, and doors closed.

5. Vehicle allowed to stand for 3 1/2 hours at lab temperatures (70-76°F).

6. After soak period, driver's side door opened and sample pump and trap placed in vehicle, trap clamped to driver's sun visor and pump started (door open approximately 10 seconds).

7. Vehicle interior sampled for 2 to 2 1/2 hours at a flow rate of 2 to 3.3 liters per minute.

8. Door opened, pump stopped, pump and trap removed from vehicle.

I. Test Sequence to Determine Influence of Vehicle Age at NEILS - Task II.

The two vehicles tested in NEILS' portion of the task were employee-owned, and tested during NEILS working hours. Nitrosamine data was available for both vehicles from previous test work. A description of the vehicles can be found in Section III-B of this report. The vehicles were tested using the following sequence:

1. Vehicles driven to NEILS parking lot by owner.

2. All windows and doors closed. Vehicles allowed to stand for 1-2 hours at ambient temperature.

3. After soak period, two sample pumps and traps placed in vehicle and pumps started. One pump and trap placed in front seat and second placed in trunk or cargo area.

4. Vehicle interior sampled at ambient temperature (27-90°F) for 4 hours at a flow rate of 2 liters per minute.

5. Pump stopped, pump and trap removed from vehicle.

J. Test Sequence to Determine Influence of Operation - Task III

Twelve vehicles were tested in Task III to determine the influence of operation on interior nitrosamine concentrations. The vehicles tested included 2 and 4 door sedans, 2 and 4 door hatchbacks, a station wagon, a pickup truck, a van and a heavy-duty truck. The vehicles tested in the task are described in detail in Section III-C of this report. All twelve vehicles were rented locally, and had less than 13,000 miles on the odometer. The vehicles were sampled at three test points: 1) immediately before operation, 2) during operation, and 3) immediately after operation.

The twelve vehicles were sampled immediately before operation using the following sequence:

1. Vehicle driven into the Emissions Lab.

2. Vehicle interior air blown out with a fan to remove all traces of nitrosamines that could have previously accumulated.

3. All doors and windows closed.

4. Vehicle allowed to stand overnight (14 to 16 hours) at lab temperature (70-76°F).

5. After overnight soak period, the driver's side door opened, pump and trap placed in the vehicle, trap clamped to the driver's sun visor and pump started (door open 10 to 30 seconds).

6. Vehicle interior sampled for 2 to 2 1/2 hours at a flow rate of 2 to 4 liters per minute.

7. Door opened, pump stopped, pump and trap removed from vehicle.

8. Door closed.

All of the vehicles with the exception of a heavy-duty truck (International Transtar II) and a Mercury Marquis were tested during operation using the following sequence:

1. Five to fifteen minutes after completion of before-operation test, driver enters vehicle with pump and trap.

2. All doors and windows closed for duration of test.

3. Trap clamped to the driver's sun visor.

4. Engine and pump started simultaneously.

5. Vehicle driven over predetermined course for 165 to 235 minutes while sampling at 2 to 4 liters per minute. Course covered approximately 125 miles with average course speed of 35 miles per hour. (Air conditioner used intermittently during test for first six vehicles. Air conditioner and heater off for duration of test for last six vehicles).

6. Vehicle returned to Emissions Lab, pump and engine stopped simultaneously.

7. Driver exits vehicle and closes door.

The testing for the International was identical except for the driving course. The International was driven over a different course to better simulate the route of a heavy-duty truck. The course for the International consisted of predominately highway driving, and covered 150 miles. The average course speed during the test was 50 miles per hour. For the Mercury Marquis, four samples were taken during operation instead of the usual one. The four samples were taken using the previously described sequence with the following variations:

1. Engine and pump No. 1 started simultaneously.

2. Pump No. 2 started 1 minute into the trip.

3. Pump No. 3 started 5 minutes into the trip.

4. Pump No. 4 started 10 minutes into the trip.

5. Engine and four pumps stopped simultaneously.

The twelve vehicles were tested immediately after operation as follows:

1. Five to fifteen minutes after completion of during operation test, driver's side door opened, pump and trap placed in vehicle, trap clamped to the driver's sun visor and pump started (door open 10 to 30 seconds).

2. Vehicle interior sampled for 2 to 2 1/2 hours at a flow rate of 2 to 4 liters per minute.

3. Door opened, pump stopped, pump and trap removed from vehicle.

K. Test Sequence to Determine Influence of Ambient Conditions - Task IV

To determine the effect of ambient temperature, fifteen vehicles were sampled in an initial screening process at the EPA-Ann Arbor lab. A description of the vehicles can be found in Section III-D of this report. The fifteen vehicles were tested at ambient lab temperatures (72-73°F) in the EPA lab soak area as follows:

1. Vehicle brought into EPA soak area.

2. Vehicle allowed to stand at lab temperature for 5 to 15 hours with driver's window open.

3. Interior air blown out with fan to remove all traces of nitrosamines that could have previously accumulated.

4. All windows and doors closed.

5. Vehicle allowed to stand for 2 to 2 1/2 hours at lab temperature (72-73°F).

6. After soak period, driver's side door opened, pump and trap placed in vehicle, trap clamped to the driver's sun visor and pump started (door open approximately 10 seconds).

7. Vehicle sampled for 1 1/2 hours at a flow rate of 2 liters per minute.

8. Door opened, pump stopped, pump and trap removed from vehicle.

Nine of the fifteen vehicles were selected for testing at 40° and 100°F. The vehicles were tested in the EPA cold room or in the EPA temperature-controlled evaporative shed. Both rooms have facilities for below- and above-ambient-temperature vehicle testing. The nine vehicles were tested in a manner similar to the ambient testing. The following sequence was used for testing at 40° and 100°C.

1. Vehicle brought into cold room or evaporative shed.

2. Vehicle allowed to stand at 40°/100° for 2 to 10 hours with all windows open.

3. Interior air blown out with fan to remove all traces of nitrosamines that could have previously accumulated.

4. All windows and doors closed.

5. Vehicle allowed to stand for 2 1/2 hours at 40°/100°.

6. After soak period, driver's side door opened, pump and trap placed in vehicle, trap clamped to the driver's sun visor and pump started (door open approximately 10 seconds).

7. Vehicle sampled for 1 1/2 hours at a flow rate of 2 liters per minute.

8. Door opened, pump stopped, pump and trap removed from vehicle.

L. Test Sequence for Additional Assessment - Task V

Twenty-five vehicles were tested as an additional assessment in Task V. The vehicles tested included three used heavy-duty trucks, six new heavy-duty trucks, six vans, five station wagons, and four motor homes. A list of the vehicles tested can be found in Section III-E of this report. With the exception of the four motor homes, two vans (Volkswagen and GMC vans), and one station wagon (Chrsyler Lebaron), all of the vehicles were tested at the SwRI Emissions Lab. The motor homes, two vans, and the one station wagon were tested on dealer lots.

The vehicles were sampled at the Emissions lab using the following test sequence:

1. Vehicle driven into the Emissions lab.

2. Vehicle allowed to stand for one hour with windows open.

3. Interior air blown out to remove all traces of nitrosamines that could have previously accumulated.

4. All windows and doors closed.

5. Vehicle allowed to soak overnight (15 hours) at lab temperature (70-76°F).

6. After soak period, the driver's side door was opened and the pump and trap were placed in the vehicle, trap clamped to driver's sun visor and pump started (door open 10 to 30 seconds). Figure 3 shows a sample cartridge being clamped to the sun visor of a heavy-duty truck.

7. Vehicle interior sampled for 2 1/2 to 4 hours at a flow rate of 2 to 4 liters per minute.

8. Door opened, pump stopped, pump and trap removed from vehicle.

Figure 3. Trap being clamped to sun visor in heavy-duty truck

The four motor homes, the GMC and Volkswagen vans, and the Chrysler Lebaron station wagon were tested on the dealer lots using the following test sequence:

1. Vehicle blown out with fan to remove all traces of nitrosamines that could have previously accumulated.

2. All windows and doors closed.

3. Vehicle allowed to stand overnight (13-18 hours) at ambient temperature (40 to 70°F).

4. After soak period, the driver's side door opened, pump and trap placed in vehicle, trap clamped to driver's sun visor and pump started (door open approximately 10 seconds).

5. Vehicle interior sampled for 2 hours at a flow rate of 2 to 4 liters per minute.

6. Door opened, pump stopped, pump and trap removed from vehicle.

III. RESULTS

This section describes the results for each of the six tasks in this program. Task I includes the peer review of the NEILS methodology for analyzing nitrosamines in car interiors and the results for determining the nitrosation potential of the ambient air, the levels of nitrosatable amines in the ambient air, and background levels of nitrosamines in the ambient air. Tasks II through IV include the results for the vehicles sampled to determine the effects of time (vehicle age), operation, and temperature on interior nitrosamine levels. Task V includes the results for vehicles sampled as an additional assessment. The vehicle types sampled in this task include new and used heavy-duty trucks, new vans, new motor homes, and new station wagons. Task VI gives a rough estimate of the exposure of several population categories to nitrosamines from vehicle interiors.

A. Task I - Sampling and Analysis Methodology

To insure the technical integrity of the data that would be generated in subsequent tasks, a peer review of the methodology used by Dr. Fine, et al, of the New England Institute for Life Sciences (NEILS), for sampling and analysis of nitrosamines was conducted. It was tentatively planned to use this methodology in the program. This peer review was conducted with the aid of other researchers (EPA and industry) who have had experience with the measurement of nitrosamines. If the methodology was found to be acceptable to the scientific community, then samples would be collected from vehicle interiors and sent to NEILS for analysis. This analysis was to be carried out at NEILS due to the relatively brief duration of the project and the relatively long set-up time needed for the methods.

To determine if the methodology was acceptable, fifteen researchers in the nitrosamine field were contacted by letter. These fifteen researchers included people who have evaluated the ThermoSorb/N Air Sampler as to recovery, efficiency, artifact formation, and other performance characteristics; as well as other researchers who have had experience with nitrosamine analysis. Individuals on the list include those known to the author who have had experience in the nitrosamine field and those recommended by Dr. Fine of NEILS and Dr. Robert Lyle of Southwest Research Institute. Dr. Lyle has had experience with nitrosamine analysis and is familiar with workers in the field. The letters sent to the researchers asked for comments on the TEA analyzer and the ThermoSorb/N Air Sampler. There were eleven responses to the letters. Table 1 lists the researchers that were contacted and their organizations, the researchers that responded, and whether or not the researchers have had experience with the TEA analyzer and/or the ThermoSorb/N Air Samplers. The responses of the contacted researchers are described in the following paragraphs.

TABLE 1. LIST OF RESEARCHERS

Researchers Contacted	Organization	Response	Experience with TEA Analyzer	Experience with ThermoSorb/N Trap
Dr. Steve Prescott	Air Products	No	--	--
Warren Hendricks	OSHA	No	--	--
Dr. Bertold Speigelhalder	Inst. fur Toxicol. und Chem., Germany	Yes	Yes	Yes
Dr. Pieter Schuler (Response by Dr. E. Ellen)	Rijksinstitunt voor de Volksgeyondkeid, Netherlands	Yes	Yes	Yes
Steve Swarin	General Motors	Yes	Yes	Yes
Dr. Edo Pellizzari	Research Triangle Institute	Yes	No	No
Dr. Tom Guley	Goodyear Tire & Rubber Co.	Yes	Yes	Yes
Dr. Roy Zweidinger (and Dave Dropkin)	EPA-RTP	Yes	No	No
Gene Weaver (Response by Mike Kelly)	Ford Motor Co.	Yes	No	Yes
Dr. Richard Leoppky	University of Missouri at Columbia		Out of Country	
Dr. S. R. Tannenbaum	Massachusetts Institute of Technology	Yes	Yes	Yes
Dr. Sidney Mirvish	Eppley Institute for Research in Cancer	Yes	Yes	--
Dr. Larry Keefer (Response by Tom Hansen)	National Institute of Health	Yes	Yes	Yes
Dr. Wm. Lijinsky	Frederick Cancer Research Center	Yes	Yes	No
Dr. Christopher Michedja	Frederick Cancer Research Center	No	--	--

Dr. Steve Prescott, Air Products, Warren Hendricks, OSHA, and Dr. Christopher Michedja, Frederick Cancer Research Center did not respond. Dr. Richard Leoppky, University of Missouri, was out of the country at the time of the review. Dr. Edo Pellizzari, Research Triangle Institute, and Dr. Roy Zweidinger (and Dave Dropkin), EPA-RTP did not have experience with the TEA analyzer or the ThermoSorb/N Air Sampler. Dr. Pellizzari, while not familiar with potential TEA and ThermoSorb/N problems, pointed out that they have been discussed by other investigators in recent publications, and suggested a careful search in analytical journals for the past two years for more information. Mike Kelly (responding for Gene Weaver), Ford, did not have experience with the TEA analyzer. However, Ford has collected samples in ThermoSorb/N traps and sent them to Dr. Fine at NEILS for analysis. In general, Mike Kelly was satisfied with Dr. Fine's methodology, however, he questioned the precision of the method at low nitrosamine concentrations and noted that Ford has observed blank ThermoSorb traps that were reported to contain trace amounts of nitrosamines. Ford has also noted in replicate testing variations of ±50 percent at low nitrosamine levels.

Dr. Sidney Mirvish, Eppley Institute for Research in Cancer, saw no need to check Dr. Fine's method since it was published in a reputable journal and peer-reviewed. Tom Hansen (responding for Dr. Larry Keefer), National Institute of Health, had used a GC-TEA and a LC-TEA. He thought the TEA sensitivity was very good (much better for GC-TEA than for LC-TEA) and was happy with the overall performance of the instrument. Mr. Hansen had little experience with the ThermoSorb/N traps, but thought that more experiments needed to be done to determine whether or not artifact formation took place on the traps. Dr. William Lijinsky, Frederick Cancer Research Center, had also worked with the TEA analyzer, but had no experience with the ThermoSorb/N traps. Dr. Lijinsky thought that the TEA analyzer was a very sensitive, useful instrument that correlated well with other GC methods of detection such as the nitrogen/phosphorus detector (NPD) and the flame ionization detector (FID). He noted that there are several compounds that interfere with the method, such as nitrite and nitrate esters which are present in smog.

Dr. S. R. Tannenbaum has had several years experience with the TEA analyzer and found it relatively trouble free with few difficulties. Dr. Tannenbaum has used the TEA analyzer for routine analysis as opposed to mass spectroscopy which is only used for confirmation. He felt the TEA is a better analyzer for quantification than mass spectroscopy. Dr. Tannenbaum has had little experience with the ThermoSorb/N traps, however he has not encountered any problems with their use.

In Dr. E. Ellen's lab (responding for Dr. Pieter Schuler), Rijksinstitunt voor de Volksgeyondkeid, Netherlands, two TEA analyzers have been used for nitrosamine analyses, one coupled to a GC and one to a HPLC. In 1976 and 1977 they performed numerous analyses using both the GC-TEA and GC-High Resolution Mass Spectroscopy. In most cases they

found good agreement between the two methods, both qualitatively and quantitatively. They have used several methods to collect nitrosamines; wet trapping (KOH solution or low temperature traps), activated charcoal, and ThermoSorb/N traps. The ThermoSorb/N sampling tubes gave better results than any other system that they have used. They observed no artifact formation of NDMA on the traps when sampling air containing 1 ppm NO/NO_2 and dimethylamine. For seven nitrosamines (NDMA, NDEA, NDPA, NDBA, NPYR, NPIP, and NMOR) they found recoveries of 80-110% when sampling 120 liters of air containing 200 ng of each nitrosamine. The other methods for trapping nitrosamines had low recoveries and/or severe artifact formation.

Dr. Bertold Spriegelholder, Inst. fur Toxicol und Chem., Germany, was very satisfied with the TEA and the ThermoSrob/N traps. He reported that the TEA instruments were easy to maintain and operate. Dr. Spriegelholder has never observed a negative mass spetrcoscopy analysis when he had found a positive TEA response. Originally, his lab analyzed every sample by both the TEA analyzer and a mass spectrometer. They found that the results from the two methods usually did not differ by more than 10-20 percent, and that the TEA was much easier to use for routine sample analysis. Nitrosamine recoveries using the ThermoSorb/N Air Sampler in his lab ranged from 90 to 100 percent. He also noted that when the traps were eluted with solvent, some sulfamic acid was removed from the traps. The material caused problems by plugging syringes in automatic samplers. They now filter all samples to prevent this problem.

Dr. Thomas Burley, Goodyear Tire and Rubber Co., has had excellent performance from both the ThermoSorb/N traps and the TEA instrument for over a year. He has found that the instrument gives linear response in the ppb range. Dr. Gurley also found that nitrosamine standards must be stored in light-protected vessels in the freezer to maintain sample integrity. His lab has found the detection limits for several nitrosamines to be as follows: 14 nanograms NDMA, 20 nanograms NDEA, and 48 nanograms NMOR per trap. Dr. Gurley feels that these limits are conservative and can be improved upon by optimizing instrument parameters. He has also found that the ThermoSorb/N traps give results that correlate well with the KOH (1.0 N) impinger traps. Dr. Gurley feels that "...the sampling technique and the analytical methodology are excellent approaches to this complex analytical problem."

Steve Swarin, General Motors, has had considerable experiences with the TEA analyzer. He has found that the instrument a) has little down time, b) is a good instrument for a technical level person to operate, c) gives a short analysis time compared to the mass spectrometer, d) correlates well with the mass spectrometer, ±20 percent, e) has good repeatability, and f) can detect nitrosamine levels from 0.002-0.2 ppb when 500 liters of air are sampled. Mr. Swarin has found that the ThermoSorb/N traps are: a) easy to use, b) stable for 3 to 4 weeks, c) have no problems when sampling at 3 liters/minute, d) have good

trap-to-trap reproducibility, and e) can be eluted with one milliliter of acetone to give 98 percent of the nitrosamines on the trap.

The above responses for the most part indicate an acceptance of the TEA analyzer and ThermoSorb/N traps by the scientific community. Researchers using both the TEA analyzer and ThermoSorb/N traps feel that both are the best available for routine analysis work. Due to the general positive nature of these responses, the ThermoSorb/N Air Samplers were used to collect nitrosamine samples from vehicle interiors and were sent to NEILS for analysis by GC-TEA.

In order to determine if sampling artifacts are being formed and to obtain information as to the origin of the nitrosamines, the level of nitrosation potential of the air, the level of nitrosatable amines in the air, and the level of nitrosamines in the ambient air were determined during the course of Tasks II, III, IV, and V.

The nitrosation potential of the ambient air (potential of the ambient air to convert amines to nitrosamines) was determined using ThermoSorb/N Air Samplers which were spiked at NEILS with the easily-nitrosated amine, morpholine. Samples were collected by SwRI and returned to NEILS for analysis of N-nitrosomorpholine. NEILS had previously found that the nitrosation potential of the air expressed in ppm NO_2 was related to the amount of N-nitrosomorpholine found in the ThermoSorb/N traps. NEILS also found that NO levels did not decrease after passage through cartridges containing morpholine, suggesting that NO does not contribute to the formation of NMOR. The following formula related the ppm NO_2 in the ambient air to the mg of N-nitrosomorpholine in the ThermoSorb/N trap.

$$\text{ppm } NO_2 = \frac{\text{Mol. Wt. } NO_2}{\text{Mol. Wt. NMOR}} \times \frac{\mu\text{g of formed NMOR}}{\text{liters of air sampled}} \times$$

$$\frac{24.45}{\text{Mol. Wt. } NO_2} \times \frac{760 \text{ (mm Hg)}}{P_{exp} \text{ (mm Hg)}} \times \frac{T(^\circ C)+273^\circ}{298^\circ K} \times$$

$$\frac{1}{0.07^*}$$

*Experimentally 6-8% of the NO_2 in the gas stream combines with the surface-held morpholine to form N-nitrosomorpholine when the traps have air containing NO_x drawn through them at 1 ℓ/min for 50 minutes.

Twenty-one nitrosation potential samples and two blanks were collected and/or analyzed during the course of the program. Table 2 lists the location from which the nitrosation potential samples were taken, the ng of NMOR found in the sample when analyzed by NEILS, the concentration of NO_2 in the ambient air using the above formula, and the ppm NO_x in the ambient air analyzed by the use of a chemiluminescent analyzer at SwRI.

TABLE 2 . NITROSATION POTENTIAL ANALYSES

Location	Date	ng NMOR per cartridge	ppm NO_2[a] calculated from trap analysis	ppm NO_x (measured)
EPA Soak Area	6/7/80	377	0.020	
Blank	6/7/80	793		
EPA Cold Room (40°)	6/12/80	177	0.005	
EPA Cold Room (100°)	6/12/80	365	0.024	
EPA Modified Cold Room (38°)	6/14/80	223	0.012	
SwRI Soak Area	8/11/80	440	0.028	< 1
Ford Mustang (After Operation	10/2/80	1400	0.048	
Chevrolet Chevette (Before Operation)	10/3/80	1270	0.043	
International Transtar II	1/9/81	1900	0.089	< 1
GMC Astro	1/13/81	2120	0.126	< 1
Blank	1/28/81	1530		
SwRI Soak Area[b]	2/11/81	118000	1.161	
Oldsmobile Cutlass Cruiser[b]	2/11/81	6720	0.063	
Ford Granada (During Operation)	2/18/81	1540	0.093	
SwRI Soak Area[c]	2/20/81	2540	0.156	< 0.5
Mercury Marquis[c]	2/20/81	2260	0.136	< 0.5

TABLE 2 (Cont'd). NITROSATION POTENTIAL ANALYSES

Location	Date	ng NMOR per cartridge	ppm NO_2[a] calculated from trap analysis	ppm NO_x (measured)
Ford Pinto (sixth sampling)	2/23/81	2130	0.145	
Winnebago Chieftain	3/17/81	1570	0.105	
Dealer Lot San Antonio[d]	3/18/81	1820	0.110	
Itasca Sunflyer[d]	3/18/81	1990	0.134	
Ford Fairmont[e]	4/23/81	600	0.018	
Oldsmobile Station Wagon[e]	4/27/81	450	0.014	
Oldsmobile Station Wagon[e]	4/27/81	510	0.015	

[a] ppm NO_2 calculated from formula

$$ppm = \frac{M.W.\ NO_2}{M.W.\ NMOR} \times \frac{\mu g \text{ of formed NMOR}}{\text{liters of air sampled}} \times \frac{24.45}{M.W.\ NO_2} \times \frac{760}{P} \times \frac{T + 273}{298} \times \frac{1}{0.07*}$$

*Experimentally 6-8% of the NO_2 in gas stream combines with the surface held morpholine to form N-nitrosomorpholine when the devices have air containing NO_x drawn through them at 1 ℓ/min for 50 min.

[b] Samples taken simultaneously
[c] Sample volume 300ℓ instead of 50ℓ
[c] Samples taken simultaneously
[d] Samples taken simultaneously
[e] Samples taken at NEILS by NEILS

The NO_2 levels in vehicle interiors were found to range from 0.014 to 0.145 ppm NO_2, while ambient air samples outside the vehicles were found to range from 0.005 to 1.161 ppm NO_2. However, the sample which gave 1.161 ppm NO_2 was inadvertantly sampled for 300 liters instead of the usual 50 liters. This longer sampling period may negate the validity of the NO_2 calculation. Disregarding this value, the NO_2 levels ranged from 0.005 to 0.156 ppm. Two blank samples were taken during the course of the program. The analyses of these two blanks at NEILS gave appreciable amounts of NMOR in each sample, 793 ng in the June 7th sample and 1530 ng in the January 28th sample. This indicates that there is some conversion of morpholine to NMOR with time (increase from 793 to 1530 ng NMOR) in a closed cartridge. Also the presence of 793 ng NMOR in the June 7th blank (higher than all samples taken in June) indicates there are problems with conversion of morpholine to NMOR during morpholine spiking or during sample analysis. The chemiluminescent NO_x measurements were accurate to only ±0.3 ppm NO_x and indicated NO_x levels less than 1 ppm. This is in agreement with the NO_2 values calculated from the NMOR levels.

The level of nitrosatable amines in the air was determined by collecting amine air samples in ThermoSorb/amine air cartridges at SwRI and EPA-AA and then sending the cartridges to NEILS where they were backflushed with 2 mℓ of 1 N KOH to elute the amines, and analyzed by injecting a portion of the eluate into a prototype TEA analyzer operating in the nitrogen mode. A minimum number of samples were collected in impingers containing dilute sulfuric acid, and analyzed using a gas chromatograph (GC) equipped with an ascarite-loaded precolumn and a nitrogen phosphorus detector (NPD). These samples were collected simultaneously with those collected in air cartridges and were analyzed at SwRI. This method is described in detail in the EPA report, "Analytical Procedures for Characterizing Unregulated Pollutant Emissions from Motor Vehicles."(4)

During the program, eighteen amine air samples and one blank cartridge were sent to NEILS for analysis. Table 3 lists the location and the date the samples were taken, the volume of air sampled, the mass (in ng) of amines found in each cartridge, the concentration of amines (in $\mu g/m^3$) determined using the sulfuric acid impinger and GC-NPD. Ten sample cartridges were found to contain dimethylamine at levels ranging from 460 to 5400 ng. These values give ambient air concentrations that range from 1 to 31 μg DMA/m^3. Morpholine was detected in four cartridges at levels ranging from 240 to 10930 ng (1 to 23 $\mu g/m^3$) and n-propylamine was detected in one cartridge (266,000 ng; 839 $\mu g/m^3$). Five samples contained one or two unknown nitrogen-containing compounds at levels ranging from 640 to 128,000 ng. These values were determined by quantification against morpholine. The Fairmont and Chevette samples which contained the n-propylamine and the highest levels of unknown compounds were inadvertantly analyzed for nitrosamines before the amine analysis. Therefore, these two samples were handled in a manner differently from the other samples. Four of the samples were collected in duplicate, one with the

TABLE 3. AMINE ANALYSES

Location	Date	Volume Sampled (liters)	ng Amine per Cartridge[a]	Amine levels µg/m^3	SwRI Amine Analysis µg/m^3
EPA Soak Area	6/7/81	163	1900 DMA[b]	12 DMA	
EPA Cold Room (105°F)	6/11/80	177	5400 DMA 240 MOR[c]	31 DMA 1 MOR	
EPA Cold Room (38°)	6/13/80	194	2700 DMA	14 DMA	
EPA Modified Cold Room (38°)	6/14/80	182	1600 DMA	9 DMA	
SwRI Soak Area	8/11/80	270	1860 MOR	7 MOR	
Fairmont (Before Operation)[g]	10/1/81	317	5400 DMA 266,000 nPrA[d] 5400 Unkn-1[e] 23,400 Unkn-2[e]	17 DMA 839 nPrA 17 Unkn-1 74 Unkn-2	
Chevette (Before Operation)[g]	10/3/81	409	720 DMA 128,000 Unkn-1 86,400 Unkn-2	2 DMA 313 Unkn-1 211 Unkn-2	
International Transtar	1/8/81	210	6800 DMA 8,600 Unkn-1 17,200 Unkn-2	32 DMA 41 Unkn-1 82 Unkn-2	14 MMA[f]
GMC Astro	1/13/81	111	720 DMA 1,980 Unkn-1	6 DMA 18 Unkn-1	2 DMA
Blank	1/28/81	--	ND	ND	

TABLE 3 (Cont'd). AMINE ANALYSES

Location	Date	Volume Sampled (liters)	ng Amine per cartridge	Amine levels µg/m^3	SwRI Amine Analysis µg/m^3
Oldsmobile Cutlass Cruiser	2/11/81	355	ND	ND	ND
Datsun 310 GX	2/16/81	315	ND	ND	
SwRI Soak Area	2/17/81	371	ND	ND	
Ford Super Wagon	2/17/81	480	640 Unkn-2	1 Unkn-2	
Ford Granada (After Operation)	2/18/81	310	ND	ND	0.1 DMA
Ford Pinto	2/23/81	347	ND	ND	
Winnebago Chieftain	3/17/81	245	ND	ND	
Ford Fairmont[h]	4/23/81	480	460 DMA 1090 MOR	1 DMA 23 MOR	
Oldsmobile Station Wagon[h]	4/27/81	480	460 DMA 3050 MOR	1 DMA 6 MOR	

[a]Detection limit 100 ng of each amine per cartridge
[b]DMA = dimethylamine
[c]MOR = morpholine
[d]nPrA = n-propylamine
[e]UnKn-1, UnKn-2, unknown compounds quantified against morpholine
[f]MMA = monomethylamine
[g]These two samples were inadvertantly analyzed at NEILS for nitrosamines before the amine analysis
[h]Samples taken at NEILS by NEILS

air cartridges, and one with sulfuric acid. In the International Transtar, SwRI (using the sulfuric acid collection media and the GC-NPD for analysis) found 14 $\mu g/m^3$ monomethylamine, while the cartridge analyzed at NEILS indicated 32 $\mu g/m^3$ dimethylamine. In the GMC Astro, both methods indicated dimethylamine (6 $\mu g/m^3$ NEILS, 2 $\mu g/m^3$ SwRI). SwRI found 0.1 $\mu g/m^3$ dimethylamine in the Ford Granada where none was detected in the corresponding air cartridge. However, the detection limit for the cartridge is calculated to be only 0.3 $\mu g/m^3$ for the sample.

To determine if nitrosamines were present in the ambient air or were present as impurities in the analysis, fourteen background and blank nitrosamine cartridges were collected and analyzed during the program. The results of these analyses are presented in Table 4. Of the thirteen, only three samples were found to contain nitrosamines (one contained 9 ng NDMA, in only one of two analyses performed on the sample; the second contained 5.4 ng NDMA which was only 0.4 ng above the minimum detection value; and the third contained 18 ng NMOR). The three traps were taken inside the EPA cold room at 105°F with two vehicles in the room; in the SwRI soak area with no test vehicles present; and in the SwRI soak area with two test vehicles present.

For additional confirmation of the presence of NDMA in vehicle interiors, three composite samples were analyzed with the aid of gas chromatography-high resolution mass spectroscopy. The following vehicle interior samples were combined to make up the three composite samples:

Sample #1 - Composite of 12 samples from heavy-duty truck interiors

Sample #2 - Composite of 20 samples from passenger car interiors

Sample #3 - Composite of 25 samples from station wagon interiors.

The composite samples were analyzed with the use of a GC-TEA before mass spectral analysis. The mass spectral analysis confirmed the presence of NDMA in vehicle interiors and was in good agreement with the GC-TEA analysis (Table 5).

B. Task II - Influence of Vehicle Age

This section describes the results for sampling four vehicles (two at SwRI and two at NEILS) once a month for 6 months during the course of the program. At SwRI, four vehicles were sampled in an initial screening process. A description of these four vehicles is presented in Table 6. The table lists the vehicle, the date the vehicle was manufactured, the mileage on the vehicle odometer during sampling, and a description of the spare tire and the vehicle interior. These parameters may influence the vehicle interior nitrosamine concentrations and are therefore recorded. The results for sampling during the SwRI screening process are presented in Table 7. Of the four vehicles, the Datsun 310 GX and the Ford Pinto

TABLE 4. BACKGROUND AND BLANK NITROSAMINE SAMPLES

Location	Date	Temp.	Volume Sampled	GC-TEA Analyses First	GC-TEA Analyses Second
EPA Soak Area	6/06/80	73°	90 ℓ	ND	ND
EPA Soak Area	6/07/80	72°	242 ℓ	ND	ND
Blank	6/07/80			ND	ND
EPA Cold Room	6/11/80	105°	178 ℓ	ND	9 ng NDMA
EPA Modified Cold Room	6/11/80	101°	164 ℓ	ND	ND
EPA Cold Room	6/12/80	100°	178 ℓ	ND	ND
Blank	6/14/80			ND	ND
SwRI Soak Area	8/06/80	81°	301 ℓ	ND	--[a]
SwRI Soak Area	10/30/80	74°	289 ℓ	ND	--[a]
SwRI Soak Area	1/20/81	73°	356 ℓ	5.4 ng NDMA	--[a]
SwRI Soak Area	1/27/81	74°	315 ℓ	18. ng NMOR	--[a]
SwRI Soak Area	1/29/81	75°	288 ℓ	ND	--[a]
SwRI Soak Area	2/12/81	70°	240 ℓ	ND	--[a]
Blank	4/27/81			ND	--[a]

[a] second analysis not conducted

TABLE 5. MASS SPECTRAL ANALYSES

Sample	GC-TEA NDMA µg/mℓ	GC-MS NDMA µg/mℓ
Composite #1	0.19	0.2
Composite #2	0.29	0.3
Composite #3	0.25	0.3

TABLE 6. DESCRIPTION OF VEHICLES SAMPLED IN SwRI TASK II SCREENING PROCESS

Vehicle	Date Manufactured	Mileage	Spare Tire	Interior
Datsun 310 GX	March 1980	03685	Bridgestone, steel belted radial	Red Cloth/Vinyl Blue Stripe
Oldsmobile Cutlass Supreme	January 1980	03469	Uniroyal, Temporary Use	Black Vinyl
Ford Pinto	December 1979 (Canada)	04038	Goodyear, Temporary Use (Canada)	Orange Cloth/ Vinyl
Pontiac Trans Am	October 1970	10229	Goodyear	Tan Cloth/ Vinyl

TABLE 7. NITROSAMINE SAMPLING RESULTS FOR SwRI TASK II SCREENING PROCESS

Vehicle	Date	Volume Sampled (liters)	ng NDMA[a] per cartridge	NDMA conc, ng/m^3
Datsun 310 GX	8/06/80	456	24	0.053
Oldsmobile Cutlass Supreme	8/06/80	381	12	0.031
Fort Pinto	8/06/80	277	13	0.047
Pontiac Trans Am	8/11/80	355	10	0.028

[a] NDMA was the only detectable nitrosamine found in the cartridges

gave the highest level of NDMA, and were selected for further testing. Both had approximately 0.05 $\mu g/m^3$ NDMA in the interior. Table 8 lists the results for sampling the Datsun 310 GX and the Ford Pinto six times over a period of 6 1/2 months. The results in Table 8 indicate a general trend of decreasing NDMA with mileage and time. This trend can be seen

TABLE 8. TEST RESULTS FOR NITROSAMINE SAMPLING - TASK II (SwRI)

Sample	Date	Mileage	Volume Sampled (liters)	ng DNMA cartridge	NDMA Levels $\mu g/m^3$
Pinto	8/6	4038	277	13	0.047
Pinto	9/24	5121	314	17[a]	0.054
Pinto	10/30	5939	319	7	0.022
Pinto	11/25	--	500	19	0.038
Pinto	1/7	--	318	10	0.031
Pinto	2/23	8769	317	11	0.035
Datsun 310	8/6	3685	456	24	0.053
Datsun 310	9/30	7120	254	8	0.031
Datsun 310	10/31	9429	315	7[c]	0.022
Datsun 310	11/25	--	395	11[b]	0.028
Datsun 310	1/8	13639	317	6	0.019
Datsun 310	2/16	16355	594	12	0.020

[a]
[b]Confirmed by LC-TEA to be 24 ng NDMA/cartridge
[c]Confirmed by LC-TEA to be 10 ng NDMA/cartridge
Sample also contained 10 ng of diethylnitrosamine NDEA

more clearly in Figures 4 and 5. Figure 4 is a plot of NDMA concentration versus time for the Datsun and Pinto. For the Datsun, the plot indicates a large initial drop of NDMA with time and a leveling off at 0.02 $\mu g/m^3$ after approximately 80 days. The Pinto plot is more scattered, but shows an overall decrease of NDMA with time. Figure 5, a plot of NDMA concentration versus miles driven after the initial test indicates an initial drop in NDMA concentration followed by a leveling off at 0.02 $\mu g/m^3$ after approximately 6,000 miles for the Datsun. The plot for the Pinto, as in the time plot, is scattered, but indicates a decrease in NDMA concentration with miles driven.

Table 9 gives a limited description of the two vehicles sampled with time at NEILS. Both vehicles had been sampled in an earlier program at NEILS and therefore data is available for the two vehicles over periods of 17 and 21 months. Table 10 lists the results for sampling the front seat area of the two vehicles. The vehicles were also sampled in the trunk (Fairmont) and in the cargo/back seat (Oldsmobile) areas. This data is presented in Appendix E. The results in Table 10 reveal no trend

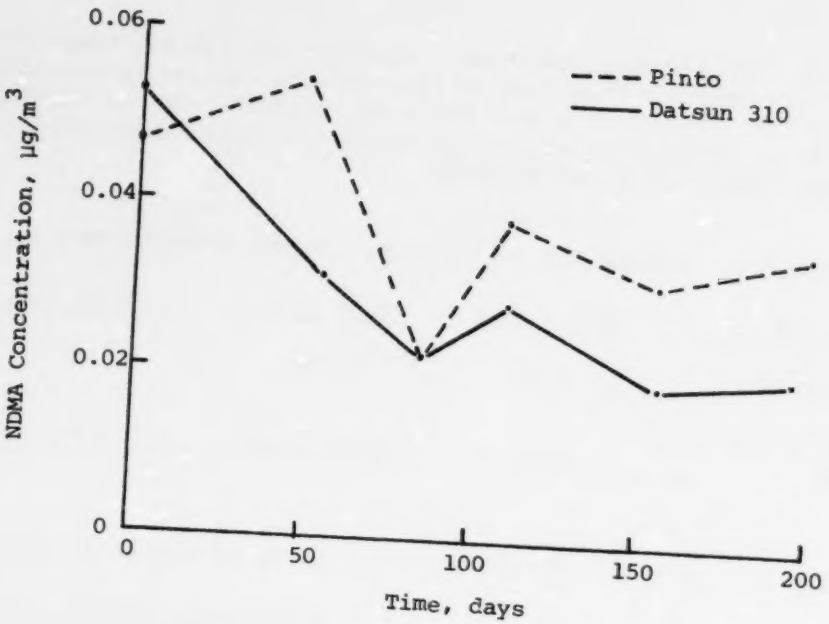

Figure 4. Plot of NDMA concentration in Ford Pinto and Datsun 310 versus time.

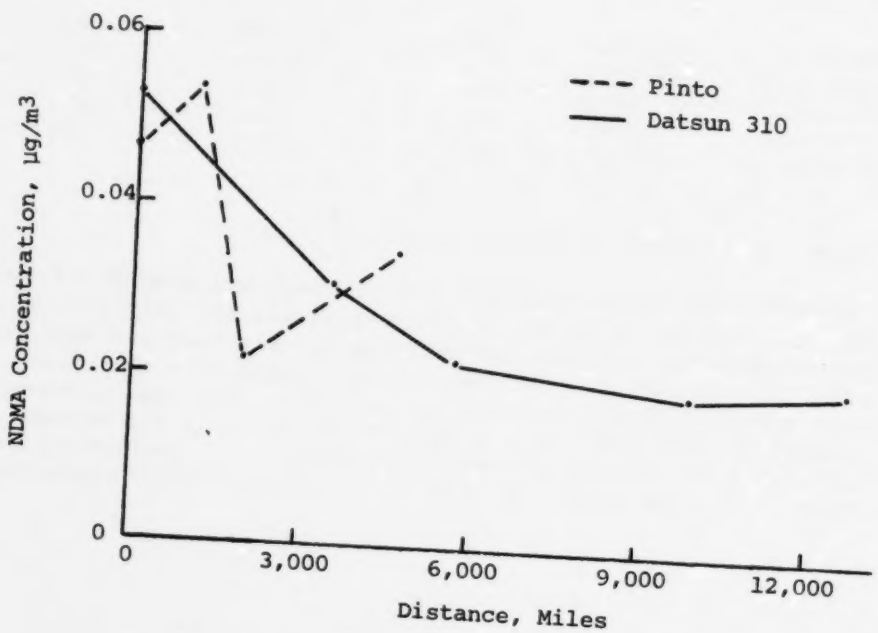

Figure 5. Plot of NDMA concentration in Ford Pinto and Datsun 310 versus distance driven.

for the nitrosamine data with time. However, the vehicle temperature was not held constant from test to test and the changes in temperature appear to have introduced a more dominant variable into the testing. Section III-D of this report presents data indicating that nitrosamine levels are dependent on temperature.

TABLE 9. DESCRIPTION OF VEHICLES SAMPLED IN NEILS TASK II

Vehicle	Model Year	Body Style	Interior
Ford Fairmont	1979	4-door	--
Oldsmobile Cutlass Supreme	1979	station wagon	tan cloth seats

TABLE 10. TEST RESULTS FOR NITROSAMINE SAMPLING-TASK II (NEILS)

Sample	Date	Temp., °F	Nitrosamine Levels, $\mu g/m^3$	
			NDMA	NMOR
Fairmont	11/2/79	45	0.059	ND
Fairmont	1/30/81	34	0.017	ND
Fairmont	2/17/81	57	0.035	ND
Fairmont	3/18/81	27	0.029	ND
Fairmont	4/23/81	64	0.083	0.098
Oldsmobile	7/23/79	90	0.244	0.360
Oldsmobile	6/17/80	75	0.180	--
Oldsmobile	2/17/81	57	0.058	ND
Oldsmobile	3/18/81	27	ND	ND
Oldsmobile	4/27/81	61	0.029	0.013

C. Task III - Influence of Operation

In this task twelve vehicles were selected and sampled to determine the influence of operation on nitrosamine levels in vehicle interiors. The twelve vehicles selected for sampling in this task are described in Table 11. Data of manufacture, mileage, spare tire description and interior description are included in the table. All twelve vehicles were rented locally and had less than 13,000 miles on the odometer. The vehicles were sampled at three test points: 1) immediately before operation, 2) during operation, and 3) immediately after operation.

TABLE 11. VEHICLES SAMPLED FOR INFLUENCE OF OPERATION

Vehicle	Body Style	Date Manufactured	Mileage	Spare Tire	Interior
Oldsmobile Cutlass Supreme	2-door	June 1980	04021	Firestone Temp. Use	Green Vinyl
Buick Skylark	4-door	March 1980	10002	General Temp. Use	Tan Cloth/Vinyl
Chevrolet Citation Hatchback	2-door	August 1979	12843	Uniroyal Hideaway	Brown/Gray Cloth Vinyl
Chevrolet Chevette Hatchback	4-door	March 1980	07385	Firestone Temp. Use	Red Vinyl
Ford Mustang	2-door	May 1980	07893	Firestone Temp. Use	Tan Cloth/Vinyl
Ford Fairmont	4-door	August 1980	00672	Michelin Radial (made in Italy)	Red Vinyl
Chevrolet Custom Deluxe	Pickup	Dec. 1979	04653	N/A	Blue Vinyl
Mercury Zephyr	Station Wagon	Dec. 1980	00349	Firestone Steel-Belted Radial	Blue Vinyl
Mercury Marquis	4-door	Sept. 1980	03007	General Dual Steel Radial	Red Cloth/Vinyl
International Transtar II	Cab over w/sleeper	Nov. 1980	01381	N/A	Tan Vinyl
Ford Super Wagon	Van	Aug. 1980	06208	Goodyear	Blue Vinyl
Ford Granada	4-door	Sept. 1980	06506	Goodyear Polysteel Radial	Tan Vinyl

To test the vehicles before operation, a vehicle was driven into the Emissions Lab, the air in the interior of the vehicle was blown out with a fan to remove any previous accumulation of nitrosamines, all doors and windows were closed, and the vehicle was allowed to soak overnight (14 to 16 hours) at lab temperature (70-76°F). After the overnight soak period, the driver's side door was opened, the pump and trap were placed in the vehicle, the trap was clamped to the driver's sun visor and the pump started. The vehicle interior was sampled for 2 to 2 1/2 hours at a flow rate of 2 to 4 liters per minute.

To test the vehicle during operation, a driver entered each vehicle with a second pump and trap five to fifteen minutes after completion of the previous test. The trap was attached as before and all doors and windows were closed for the duration of the test. The vehicle and pump were started simultaneously. The vehicle was driven over a predetermined course for 165 to 235 minutes while sampling at 2 to 4 liters per minute. The course covered approximately 125 miles with an average course speed of 35 miles per hour. Upon returning to the Emissions Lab, the pump and engine were turned off simultaneously. The International Transtar II was driven over a different course to better simulate the route of a heavy-duty truck. The course in this case consisted of predominantly highway driving with only three stops. It covered approximately 150 miles with an average speed of 50 miles per hour. The air conditioner was used intermittently during the testing of the first six vehicles. The last six vehicles were tested with all windows closed and with the air conditioner and heater off for the duration of the test. Four samples were taken during the operation of the Mercury Marquis instead of the usual one. In this case, the first sample pump and the vehicle were started simultaneously, and the second, third, and fourth pumps were started at 1, 5, and 10 minutes into the trip. All four pumps and the engine were stopped simultaneously at the end of the trip.

To test the vehicle after operation, the vehicle was driven back into the Emissions Lab and a third pump and trap were placed in the vehicle. This test was conducted as described in the "before operation test." This test began five to fifteen minutes after the completion of the previous test.

The results for samples from the twelve vehicles are listed in Table 12. All twelve vehicles were found to contain detectable concentrations of NDMA before operation, at levels of 0.013 to 0.141 $\mu g/m^3$. No other nitrosamines were detected for the before- and after-operation testing. The average levels of NDMA before operation (0.049 $\mu g/m^3$ for 12 vehicles) and after operation (0.049 $\mu g/m^3$ for 11 vehicles) were equal, indicating a relatively rapid equilibrium of NDMA between the materials in the vehicle interior and the interior air. During operation, five vehicles were found to contain nitrosamines. Two vehicles contained only NDMA, one contained NDMA and NDEA, one contained NDMA and NMOR, and one contained NDMA, NDEA, and NMOR. The presence of NDEA and NMOR is not fully understood, since these nitrosamines were not found before-

TABLE 12. TEST RESULTS FOR NITROSAMINE SAMPLING-TASK III

Vehicle	Test Condition	Volume Sampled (liters)	Nitrosamine Analysis (ng NDMA/cart.)	Nitrosamine levels ($\mu g/m^3$)
Oldsmobile Cutlass Supreme	Before Operation	355	10	0.028 NDMA
	During Operation	744	ND[a]	ND
	After Operation	353	4	0.011 NDMA
Buick Skylark	Before Operation	412	8	0.019 NDMA
	During Operation	714	ND	ND
	After Operation	415	8	0.019 NDMA
Chevrolet Citation	Before Operation	570	12	0.021 NDMA
	During Operation	810	ND	ND
	After Operation	570	13	0.023 NDMA
Chevrolet Chevette	Before Operation	500	14	0.028 NDMA
	During Operation	696	ND	ND
	After Operation	501	8	0.016 NDMA
Ford Mustang	Before Operation	435	9	0.021 NDMA
	During Operation	592	ND	ND
	After Operation	444	14	0.032 NDMA
Ford Fairmont	Before Operation	458	6	0.013 NDMA
	During Operation	693	ND	ND
	After Operation	413	ND	ND
Chevrolet Pick-Up	Before Operation	252	14	0.055 NDMA
	During Operation	631	ND	ND
	After Operation	346	14	0.040 NDMA
Mercury Zephyr Station Wagon	Before Operation	455	64[b]	0.141 NDMA
	During Operation	655	20[c] 6.9NDEA[d]	0.031 NDMA 0.011 NDEA
	After Operation	250	42[e]	0.168 NDMA

TABLE 12 (Cont'd) TEST RESULTS FOR NITROSAMINE SAMPLING-TASK III

Vehicle	Test Condition	Volume Sampled (liters)	Nitrosamine Analysis (ng NDMA/cart.)	Nitrosamine levels ($\mu g/m^3$)
Mercury Marquis	Before Operation	456	25	0.055 NDMA
	During Operation (duration of test)	708	ND	ND
	During Operation (one min. into trip)	641	11	0.017 NDMA
			18 NMOR	0.028 NMOR
	During Operation (five min. into trip)	358	ND	ND
	During Operation (ten min. into trip)	334	7.2	0.022 NDMA
			8.2 NDEA	0.025 NDEA
	After Operation	431	18	0.042 NDMA
International Transtar II	Before Operation	247	15	0.061 NDMA
	During Operation	708	5.5	0.008 NDMA
	After Operation	252	14	0.056 NDMA
Ford Superwagon	Before Operation	252	22	0.087 NDMA
	During Operation	579	30	0.052 NDMA
			21 NMOR	0.036 NMOR
	After Operation	247	18	0.073 NDMA
Ford Granada	Before Operation	247	15	0.061 NDMA
	During Operation	776	8.5	0.011 NDMA
	After Operation	248	14	0.056 NDMA

[a] Not detected - limit of detection per cartridge 5 ng for NDMA, 6.5 ng for NDEA, and 9 ng for NMOR
[b] Confirmed by LC to be 45 ng NDMA/cartridge
[c] Confirmed by LC to be 22 ng NDMA/cartridge
[d] Confirmed by LC to be 6.5 ng NDEA/cartridge
[e] Confirmed by LC to be 40 ng NDMA/cartridge

or after-operation. NDEA and NMOR were found in only one of four traps for the vehicle that contained both NDEA and NMOR. The levels of NDMA found during operation for the Zephyr station wagon, the Marquis (average of the four traps), and the Granada were approximately one fifth of those found before and after operation. The levels were higher for the Super-wagon, one half, and lower for the International Transtar II, one seventh. If the first six vehicles tested had NDMA levels during operation one fifth or less of the before- and after-operation average, then the levels would be below the detection limits of the methodology and would not be detected. No NDMA was detected during operation for the first six vehicles. If the Chevrolet Pick-up contained one seventh or less of the before and after operation average, then no NDMA would be detected (no NDMA was detected).

D. Task IV - Influence of Ambient Conditions

This section describes the results of testing new car interiors to determine the influence of ambient temperature conditions on nitrosamine levels in the car interior. In an initial screening process, fifteen new vehicles were obtained by EPA and brought to the EPA Ann Arbor lab. With the aid of EPA, SwRI sampled the fifteen vehicles at ambient lab temperature, 72-73°F. A description of the fifteen vehicles is given in Table 13. For testing at ambient temperature, the vehicles were allowed to stand at lab temperature for 5 to 15 hours with the driver's window open. The air in the interior of the vehicle was then blown out with a fan to remove all traces of nitrosamines that could have accumulated at a previous temperature. The vehicles were then closed and allowed to soak for 2 to 2 1/2 hours at lab temperature (72-73°F). After the soak period, the driver's side door was opened, the pump and trap were placed in the vehicle, the trap was clamped to the driver's sun visor and the pump started (door open approximately 10 seconds). The vehicle was sampled for 1 1/2 hours at a flow rate of 2 liters per minute.

The results for sampling the fifteen vehicles are listed in Table 14. Nine of the vehicles were selected for testing at 40 and 100°F as a result of nitrosamine detection in the first nitrosamine analysis (column 3). The nitrosamine cartridges were reanalyzed by NEILS at a later date. The results for this reanalysis are listed in column 4. In the first set of analyses, the Citation and St. Regis gave measurable amounts of NDMA and the LTD did not, whereas in the second set of analyses, the LTD gave a measurable amount of NDMA and the Citation and St. Regis did not. Because the selection of the vehicles for further testing was based on the initial analysis, the Citation and St. Regis were selected for further testing and the Ford LTD was not selected. Table 14 also lists LC-TEA confirmational analyses for seven of the samples and calculated NDMA concentrations in µg NDMA per cubic meter of air. The calculations are based on the average of the first and second GC-TEA analyses or on only one of the two analyses when the second analysis gave no detection.

TABLE 13. VEHICLES SAMPLED AT AMBIENT TEMPERATURE (72-73°F)

Vehicle	Date Manufactured	Mileage	Spare Tire	Interior
Plymouth Horizon/ Hatchback	May 1980	00062	Firestone Temp. Use	Tan Vinyl
Ford Pinto/ Hatchback	March 1980	01816	Goodyear Temp. Use	Red Vinyl
Ford LTD	March 1980	01678	Firestone Steel Belted Radial	Beige Cloth/Vinyl
Honda Accord	April 1980	00017	Bridgestone Steel Belted Radial	Tan Cloth/Vinyl
Chevrolet Caprice Classic	December 1979	07325	Uniroyal Hideaway	Blue Vinyl
Oldsmobile Cutlass Supreme	December 1979	02121	Uniroyal	Tan Cloth/Vinyl
Dodge St. Regis	January 1980	00013	Goodyear Temp. Use	Cream Cloth/Vinyl
Ford Mustang/ Hatchback	January 1980	01748	B.F. Goodrich Temp. Use	Blue Cloth/Vinyl
Dodge Diplomat/ Wagon	February 1980	00077	Goodyear Temp. Use	Tan Cloth/Vinyl
Chevrolet Citation/ Hatchback	January 1980	10670	General	Tan Vinyl
Chrysler Newport	December 1979	00212	Goodyear Temp. Use	Tan Cloth/Vinyl
Mercury Marquis	March 1980	00151	Goodyear Radial	Beige Cloth/Vinyl
Ford Mustang/ Hatchback	February 1980	00022	Firestone, Limited Use, Space Saver	Blue Cloth/Vinyl
Datsun 310 GX	January 1980	00427	Bridgestone	Blue Cloth/Vinyl
Toyota Corolla Sport Coupe	March 1980	00202	Bridgestone Steel Belted Radial	Cream/Brown Vinyl

TABLE 14. TEST RESULTS FOR SAMPLING AT 72°F-TASK IV

Vehicle	Vol. Samp. (liters)	ng NDMA/Cartridge First Analysis GC-TEA	ng NDMA/Cartridge Second Analysis[a] GC-TEA	ng NDMA/ Cartridge LC-TEA[b]	Levels, ($\mu g/m^3$)[c]
Plymouth Horizon/ Hatchback	213	ND[d]	ND		ND
Ford Pinto/ Hatchback	188	ND	ND		ND
Ford LTD	181	ND	23	19	0.127
Honda Accord	195	ND	ND		ND
Chevrolet Caprice Classic	190	ND	ND		ND
Oldsmobile Cutlass Supreme	174	ND	ND		ND
Dodge St. Regis	188	4.6	ND		0.024
Ford Mustang/ Hatchback	207	5	18	8	0.056
Dodge Diplomat/Wagon	207	9.6	6		0.038
Chevrolet Citation/ Hatchback	184	8.4	ND		0.046
Chrysler Newport	196	9.4	15	8	0.062
Mercury Marquis	207	11	26	23	0.089
Ford Mustang/ Hatchback	185	12	12	20	0.065
Datsun 310 GX	188	16	19	11	0.093
Toyota Corolla Sport Coupe	183	16	33	30	0.134

[a]Second analysis of same sample cartridges by GC-TEA, detection limit 5 ng/cartridge
[b]Confirmational analysis performed on samples by LC-TEA
[c]Levels based on the average of the first and second GC-TEA analyses or on one of the two analyses when the second analyses gave no detection
[d]No detection

The testing of the nine vehicles at 40° and 100°F was performed in a manner similar to that described for the ambient tests, with the following differences. The vehicles were allowed to stand at 40 or 100°F for 2 to 10 hours (ambient 5-15 hours) with all windows open, and after blowing out the interior air and closing all windows and doors, the vehicles were allowed to soak for 2 1/2 hours before testing (ambient 2 to 2 1/2 hours).

The nine vehicles that were selected for further study are listed in Table 15, along with the volume of air sampled from the interior, results from duplicate analyses of the ThermoSorb cartridges, and calculated NDMA concentrations. The data in Table 15 appear to indicate NDMA dependence on temperature, with higher temperatures giving higher levels of NDMA. This dependence on temperature can be seen more clearly in Figures 6 and 7. The two figures show increases in NDMA concentrations with temperature for all nine vehicles.

E. Task V - Additional Assessment

Twenty-five vehicles were sampled in this task, widening the nitrosamine data base to include new and used heavy-duty trucks, new vans, motor homes, station wagons, and pickup trucks. The vehicles sampled in this task are listed in Table 16. With the exception of the four motor homes and the Chrysler Lebaron station wagon, all vehicles tested were found to contain one or more nitrosamines at levels of 0.01 to 0.12 $\mu g/m^3$ (Table 17). The four motor homes contained no detectable concentrations of nitrosamines. The Chrysler LeBaron station wagon (1 mile on odometer) contained 0.38 $\mu g/m^3$ NDMA and 0.16 $\mu g/m^3$ N-nitrosodibutylmaine (NDBA).

The three used heavy-duty trucks contained only NDMA, at levels of 0.022 to 0.029 $\mu g/m^3$. The Ford 9000 and the White Road Boss had conventional cabs, while the Freightliner had a "cab over" with a sleeper. This testing indicated that used heavy-duty trucks, over three years old and with over 200,000 miles on the odometer, can still contain measurable amounts of nitrosamines. The six new heavy-duty trucks contained higher levels of NDMA, 0.026 to 0.119 $\mu g/m^3$, with an average of 0.067 $\mu g/m^3$. Three trucks, the two Freightliners and the Mercedes, contained only NDMA, while the two Internationals and the GMC were found to also contain NDEA and/or NMOR at levels of 0.014 to 0.104 $\mu g/m^3$. Total nitrosamine levels in the six trucks ranged from 0.026 $\mu g/m^3$ for the Mercedes to 0.151 $\mu g/m^3$ for the International S1800, with an average level of 0.091 $\mu g/m^3$. The Mercedes' interior contained little non-metallic material other than the seat. This could explain the lower nitrosamine levels for the Mercedes.

The six vans tested in the program all contained NDMA at levels ranging from 0.017 to 0.101 $\mu g/m^3$, with an average concentration of 0.041 $\mu g/m^3$. The Chevrolet Van 30 (mini school bus manufactured by Wayne Corp), the Dodge Sportsman, and the Volkswagen Vanagon contained only NDMA, while the Ford Club Wagon and the Ford Superwagon also

TABLE 15. TEST RESULTS FOR SAMPLING AT 40, 72 and 100°F

Vehicle	Temp. °F	Vol. Samp. (liters)	First Nitrosamine Analysis ng NDMA/Cartridge	Second Nitrosamine Analysis ng NDMA/Cartridge	NDMA Levels ($\mu g/m^3$)[a]
Dodge St. Regis	45	190	trace NMOR	ND[b]	ND
Dodge St. Regis	73	188	4.6	ND	0.024
Dodge St. Regis	94	181	trace	14	0.077
Chevrolet Citation	40	178	trace NMOR	ND	ND
Chevrolet Citation	72	184	8.4	ND	0.046
Chevrolet Citation	103	177	44	44	0.249
Dodge Diplomat	40	188	trace	ND	ND
Dodge Diplomat	73	207	9.6	6	0.038
Dodge Diplomat	100	188	ND	28	0.149
Ford Mustang (Man. Trans)	41	182	ND	ND	ND
Ford Mustang	72	207	5	18	0.056
Ford Mustang	100	184	trace	11	0.060
Ford Mustang (Auto. Trans)	42	192	ND	ND	ND
Ford Mustang	72	185	12	12	0.065
Ford Mustang	98	188	23	32	0.146
Chrysler Newport	45	200	ND	ND	ND
Chrysler Newport	73	196	9.4	15	0.062
Chrysler Newport	94	186	trace	23	0.124
Mercury Marquis	42	179	ND	ND	ND
Mercury Marquis	72	207	11	26	0.089
Mercury Marquis	99	180	26	30	0.156
Datsun 310 GX	41	184	ND	ND	ND
Datsun 310 GX	72	188	16	19	0.093
Datsun 310 GX	103	186	31	49	0.215
Toyota Corolla	41	190	ND	ND	ND
Toyota Corolla	72	183	16	33	0.134
Toyota Corolla	100	195	51	79	0.333

[a] Levels based on the average of the first and second analyses or on only one of the two analyses when the second analysis gave a trace amount or no detection

[b] No detection, detection limit for second analysis 5 ng NDMA/Cartridge

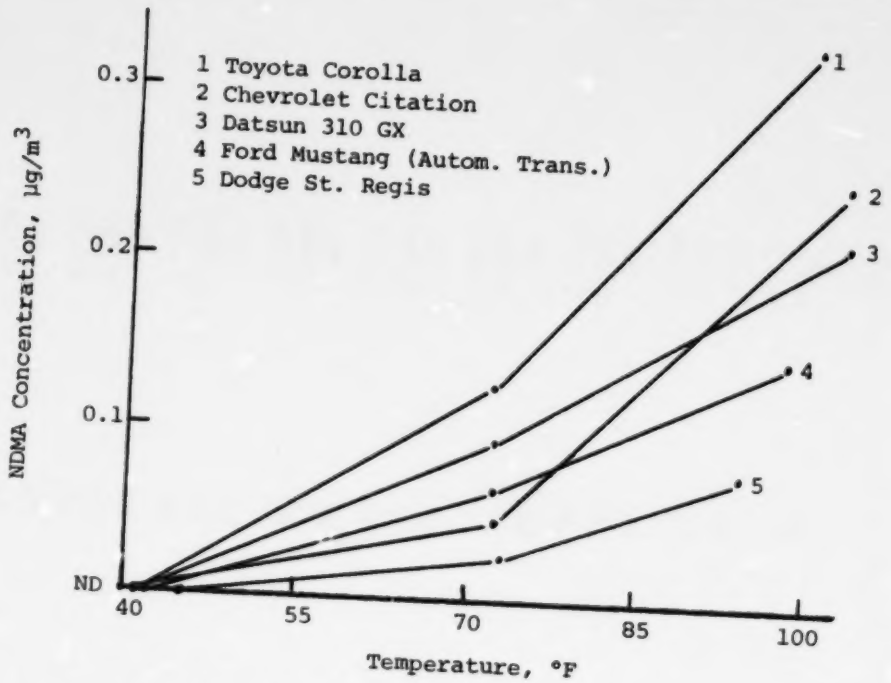

Figure 6. NDMA concentration as a function of temperature: Toyoto Corolla, Chevrolet Citation, Datsun 310 GX, Ford Mustang (Autom. Trans.), Dodge St. Regis.

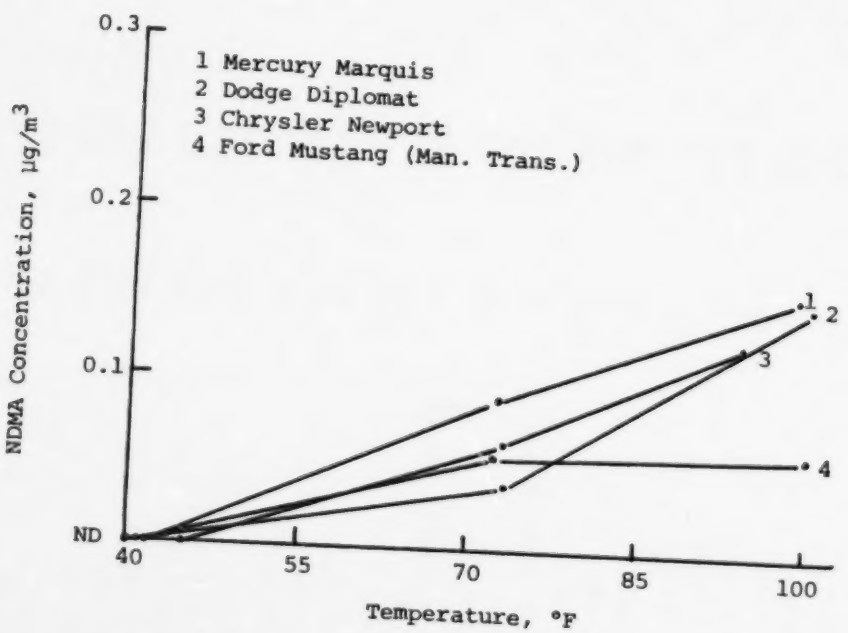

Figure 7. NDMA concentration as a function of temperature: Mercury Marquis, Dodge Diplomat, Chrysler Newport, Ford Mustang (Man. Trans.).

TABLE 16. VEHICLES SAMPLED FOR ADDITIONAL ASSESSMENT

Vehicle	Body Style	Date Manufactured	Mileage	Spare Tire	Interior
Freightliner	Cab over w/sleeper	March 1978	217,616	N/A	Dark Red Vinyl
Ford 9000	Conventional Cab	1978	103,879	N/A	Brown Vinyl
White Corp. Road Boss #2	Conventional Cab	1979	124,470	N/A	Brown Vinyl
Freightliner	Cab over w/sleeper	July 1980	46	N/A	Dark Red Vinyl/Cloth
International S 1800	Conventional Cab	September 1980	3,377	N/A	Brown Vinyl
Mercedes 116 Diesel	Conventional Cab	May 1980	250	N/A	Red/Black Vinyl/Cloth
International Transtar II	Cab over w/sleeper	October 1980	44	N/A	Tan Vinyl
GMC Astro	Cab over w/sleeper	October 1980	26	N/A	Black Vinyl
Freightliner	Cab over w/sleeper	September 1979	12,987	N/A	Dark Red Vinyl
Ford Club Wagon	4 seat van	August 1980	2,252	General, Jumbo Steel Radial	Blue Vinyl/Cloth
Ford Super Wagon	Van	October 1980	436	Goodyear	Brown Vinyl
Chevrolet Van 30	Mini Bus	March 1980	14,422	N/A	Green/Tan Vinyl
Dodge Sportsman	Van	May 1980	1,828	Goodyear	Blue Vinyl/Cloth
Volkswagen Vanagon	Van	August 1980	15	N/A	Tan Vinyl/Cloth
GMC Vandura 25	Van	October 1980	21	Uniroyal	Tan Vinyl
Ford Custom F150	Pickup	July 1980	6,461	N/A	Blue Vinyl

TABLE 16 (Cont'd). VEHICLES SAMPLED FOR ADDITIONAL ASSESSMENT

Vehicle	Body Style	Date Manufactured	Mileage	Spare Tire	Interior
Chevrolet Impala	Station Wagon	September 1980	3,530	Goodyear Convenience Spare	Tan Vinyl
Chevrolet Caprice	Station Wagon	September 1980	6,383	Goodyear Convenience Spare	Tan Vinyl
Oldsmobile Cutlass Cruiser	Station Wagon	October 1980	4,214	Uniroyal Hideaway	Tan Vinyl
Chrysler LeBaron	Station Wagon	January 1981	1	General	Red Vinyl
Mercury Marquis	Station Wagon	October 1980	2,625	General	Off-White Vinyl
Winnebago Sportscoach	Motor Home	October 1980	2,082	N/A	Orange/Tan/Cloth/ Vinyl
Winnebago Chieftain	Motor Home	December 1980	1,924	N/A	Brown Cloth
Itasca Sunflyer	Motor Home	September 1980	4,846	N/A	Blue/Beige Cloth
Winnebago Sportsman	Motor Home	October 1980	1,115	N/A	White/Orange/Brown Cloth/Vinyl

TABLE 17. TEST RESULTS FOR NITROSAMINE SAMPLING-TASK V

Vehicle	Vol. Samp. (liters)	Nitrosamine Anal. GC-TEA (ng/Cartridge)	Confirmational Anal. LC-TEA (ng/Cartridge)	Nitrosamine Levels $\mu g/m^3$
Freightliner (3/78)	697	17 NDMA	a	0.024 NDMA
Ford 9000	796	23 NDMA	a	0.029 NDMA
White Road Boss	835	18 NDMA	a	0.022 NDMA
Freightliner (7/80)	768	34 NDMA	30 NDMA	0.044 NDMA
International S1800	828	39 NDMA 86 NDEA	30 NDMA 55 NDEA	0.047 NDMA 0.104 NDEA
Mercedes 116 Diesel	770	20 NDMA	19 NDMA	0.026 NDMA
International Transtar II	683	81 NDMA 9.7 NDEA 9.7 NMOR	47 NDMA ND ND	0.119 NDMA 0.014 NDEA 0.014 NMOR
GMC Astro	607	68 NDMA 9.7 NMOR	92 NDMA 27 NMOR	0.112 NDMA 0.016 NMOR
Freightliner (9/79)	805	42 NDMA	30 NDMA	0.052 NDMA
Ford Club Wagon	536	28 NDMA 29 NMOR	25 NDMA 29 NMOR	0.052 NDMA 0.054 NMOR
Ford Superwagon	376	38 NDMA 13 NDEA	39 NDMA 12 NDEA	0.101 NDMA 0.035 NDEA
Chevrolet Van 30	376	7.3 NDMA	a	0.019 NDMA
Dodge Sportsman	648	11 NDMA	a	0.017 NDMA
Volkswagen Vanagon	464	8 NDMA	a	0.017 NDMA
GMC Vandura 25	456	19 NDMA 7.7 NDEA 21 NDPA 25 NMOR	17 NDMA ND ND 45 NMOR	0.042 NDMA 0.017 NDEA 0.046 NDPA 0.055 NMOR
Ford Custom F150	364	17 NDMA 23 NMOR	a a	0.047 NDMA 0.063 NMOR

TABLE 17 (Cont'd). TEST RESULTS FOR NITROSAMINE SAMPLING-TASK V

Vehicle	Vol. Samp. (liters)	Nitrosamine Anal. GC-TEA (ng/Cartridge)	Confirmational Anal. LC-TEA (ng/Cartridge)	Nitrosamine Levels $\mu g/m^3$
Chevrolet Impala	360	28 NDMA	24 NDMA	0.078 NDMA
Chevrolet Caprice	376	12 NDMA	a	0.032 NDMA
		15 NMOR	a	0.040 NMOR
Oldsmobile Cutlass Cruiser	626	13 NDMA	a	0.021 NDMA
Chrysler LeBaron	472	183 NDMA	116 NDMA	0.388 NDM
		14 NDEA	8.3 NDEA	0.030 NDEA
		75 NDBA	36 NDBA	0.159 NDBA
		27 NMOR	26 NMOR	0.057 NMOR
Mercury Marquis	312	35 NDMA	a	0.112 NDMA
		31 NMOR	a	0.099 NMOR
Winnebago Sports-coach	275	ND	a	ND
Winnebago Chieftain	480	ND	a	ND
Itasca Sunflyer	480	ND	a	ND
Winnebago Sportsman	253	ND	a	ND

[a]No LC-TEA confirmational analysis conducted

contained NMOR. The GMC Vandura, the only cargo van tested, contained NDMA, NDEA, NMOR, and N-nitrodipropylamine (NDPA). This was the only instance in which NDPA was detected in a vehicle interior during the entire program. However, NDPA was not detected in the LC-TEA confirmational analysis. Total nitrosamine levels in new vans ranged from 0.017 to 0.160 $\mu g/m^3$, with an average of 0.076 $\mu g/m^3$.

One pickup truck was tested in this task, a Ford Custom F150. The Ford pickup contained both NDMA and NMOR at levels of 0.047 and 0.063 $\mu g/m^3$, respectively.

Five station wagons were tested in this task. All five wagons contained NDMA at levels ranging from 0.021 to 0.388 $\mu g/m^3$ NDMA. The average NDMA level was 0.126 $\mu g/m^3$. The Caprice and Marquis also contained NMOR at 0.040 and 0.057 $\mu g/m^3$, respectively. The Chrysler LeBaron contained four nitrosamines, NDMA, NDEA, NDBA, and NMOR. All four were confirmed by LC-TEA. The total nitrosamines ranged from 0.021 $\mu g/m^3$ for the Oldsmobile Cutlass to 0.634 $\mu g/m^3$ for the Chrysler Lebaron. The average nitrosamine concentration for the five station wagons was 0.203 $\mu g/m^3$.

Four motor homes were tested in the task. None of the four had a detectable level of nitrosamines in the vehicle interior. This was the only vehicle group tested in the program in which no detectable levels of nitrosamines were found.

F. Task VI - Exposure Assessment

This section gives the results for estimating exposure levels of several population categories to nitrosamines from vehicle interiors. The respiration rate of an average male during operation of a vehicle has been estimated to be 5 to 10 liters of air per minute.(5) The upper value, 10 ℓ/min, has been used in all of the following estimates to simplify calculations. The assumption that 100% of the inhaled nitrosamines were absorbed by the body was also made.

If a commuter is exposed to nitrosamines for 3 hours/day in a moving vehicle and for 10 minutes a day in a vehicle at rest, the maximum daily exposure can be calculated using the data from Tasks III and V. The maximum concentration of nitrosamine in a vehicle interior was 0.63 $\mu g/m^3$ (Task V) and the maximum level in a moving passenger car was found to be one fifth of the at-rest concentration (Task III), or 0.13 $\mu g/m^3$ when applied to this maximum case. Using this data, the amount of nitrosamines a commuter is exposed to per day can be calculated as follows:

$$\text{mass nitrosamines} = \left(\frac{0.63\ \mu g\ \text{nitrosamines}}{m^3} \times \frac{10\ \ell}{\text{min}} \times \frac{0.001\ m^3}{\ell}\right) \times$$

$$\left[\left(1.0 \times 10\ \text{min}\right) + \left(0.2 \times 3\ \text{hr} \times \frac{60\ \text{min}}{\text{hr}}\right)\right]$$

$$= 0.3\ \mu g\ \text{nitrosamines}$$

If the average nitrosamine concentration (not including the 4 motor homes) found in the project, 0.08 $\mu g/m^3$, is used in the calculation, then the exposure to a commuter would be:

$$(0.07 \times 10 \times 0.001)\ [(1.0 \times 10) + (0.2 \times 3 \times 60)] = 0.04\ \mu g \text{ nitrosamines}$$

The data in Tasks III and V can be used to calculate other daily exposure categories, such as the truck driver. A maximum exposure case would be a truck driver who operates his truck for 16 hours and sleeps the remaining 8 hours in the truck. The highest nitrosamine concentration for a heavy-duty truck was found to be 0.15 $\mu g/m^3$ (Task V). The concentration in a moving truck was found to be one seventh of the at-rest concentration (Task III). Using these data the maximum exposure of a truck driver would be:

$$(0.15 \times 10 \times 0.001)\ [(1.0 \times 8 \times 60) + (0.143 \times 16 \times 60)] = 0.9\ \mu g \text{ nitrosamines}$$

If the average nitrosamine concentration in heavy-duty truck interiors is used, 0.09 $\mu g/m^3$, then the daily exposure would be 0.6 μg of nitrosamines. The eight hours sleeping in the truck contributes 0.4 μg of this value.

The average interior nitrosamine concentration for a van at-rest is 0.08 $\mu g/m^3$ (Task V). A van in operation contains approximately one-half the at-rest concentration (Task III). If the driver of a van is exposed to 7 1/2 hours of nitrosamines in a moving vehicle and 30 minutes in a vehicle at-rest, then the exposure would be:

$$(0.08 \times 10 \times 0.001)\ [(1.0 \times 30) + (0.5 \times 7.5 \times 60)] = 0.2\ \mu g \text{ nitrosamines}$$

A worst-case situation for daily exposure would exist for a person remaining in a closed, non-moving vehicle for 24 hours. If the highest nitrosamine concentration for a vehicle interior obtained in the program is used (0.63 $\mu g/m^3$), maximum exposure would be:

$$0.63 \times 10 \times 0.001 \times 24 \times 60 = 9\ \mu g \text{ nitrosamines}$$

IV. DISCUSSION OF THE RESULTS

The response from the scientific community for the most part indicates an acceptance of the TEA analyzer and the ThermoSorb/N traps for nitrosamine analysis and collection. Researchers who have used both the TEA analyzer and the ThermoSorb/N traps feel that both are the best available for routine nitrosamine analysis.

Of the fifty-eight vehicles sampled in the program, forty-nine contained NDMA (0.014 to 0.388 $\mu g/m^3$), fourteen contained NMOR (trace to 0.360 $\mu g/m^3$), eight contained NDEA (0.011 to 0.104 $\mu g/m^3$), one contained NDPA (0.046 $\mu g/m^3$), and one NDBA (0.159 $\mu g/m^3$). Total nitrosamine levels ranged from 0.01 to 0.63 $\mu g/m^3$. The concentrations in general are lower than those found by Fine for new 1979 passenger cars, 0.07 $\mu g/m^3$ to 2.91 $\mu g/m^3$.(1,2)

Testing in the program indicated NDMA dependence on mileage and time with NDMA levels decreasing slightly with time and mileage. It showed NDMA dependence on temperature, with higher temperatures giving higher levels of NDMA. Detectable levels of NDMA were found in vehicles during operation (e.g., one fifth of the at-rest concentration for a passenger car if all windows are closed and the air conditioner and heater off). Similar levels of NDMA were found in vehicles sampled after being closed overnight or sampled immediately after operation. NMOR and NDEA were detected randomly in the program, and no trends were observed for these nitrosamines.

Nitrosamines were found in passenger cars, station wagons, passenger and cargo vans, pickup trucks, and in new and used heavy-duty trucks. Nitrosamines were not detected in four motor homes tested in the program.

The nitrosation potential and level of nitrosatable amines of the ambient air were monitored throughout the program. No detectable nitrosamine trends with NO_2 or amines were observed in the program. Nitrosamines were found in three of eleven background nitrosamine samples taken during the program. In one background sample, NDMA was detected in only one of two duplicate analyses; in the second sample, the randomly appearing nitrosamine NMOR was detected; and in the third background sample, NDMA was detected at the detection limit of the analytical procedure.

Other common sources of nitrosamines in the environment include beer and bacon. Dr. Fine at NEILS has estimated that one can of beer contains 1 µg of nitrosamines, and one strip of bacon contains 0.1 µg of nitrosamines.(1,2) If these values are accurate and if inhalation and ingestion are comparable routes of exposure, then the average daily exposure of a commuter would be greater from either a can of beer or a strip of bacon than from a vehicle interior (0.04 µg of nitrosamines).

REFERENCES

1. Rounbehler, D. P., et al, Fd Cosmet. Toxicol., Vol. 18, pg 147, 1980.

2. Walker, E. A., et al (Ed.), N-NITROSO- Compounds: Analysis, Formation and Occurrence, International Agency for Research on Cancer, Lyon, IARC Scientific Publication No. 31, pg 541, 1980.

3. Rounbehler, D. P., et al, Anal. Chem., Vol. 52, pg 273, 1980.

4. Dietzmann, H. E., et al, "Analytical Procedures for Characterizing Unregulated Pollutant Emissions from Motor Vehicles," EPA Report 600/2-79-017, February 1979.

5. Private Communication with Jeffrey Waugh, Southwest Foundation for Research and Education, San Antonio, Texas.

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APPENDICES

A. "Instructions for Monitoring"
B. Description of the GC-MS System (as Reported to SwRI by NEILS)
C. Description of the Nitrosation Capacity Determination (as Reported to SwRI by NEILS)
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APPENDIX A

"Instructions for Monitoring"

ThermoSorb/N Air Sampler
Instructions for Monitoring

Introduction

Air is drawn through a proprietary sorbent with a suitable air sampling pump. The N-nitroso compounds are absorbed with high efficiency. After sampling is complete, the sorbent is eluted with solvent to remove the N-nitroso compounds. The solvent is then analyzed by combined gas-liquid chromatography with TEA Analyzer. Detection limits of better than 0.05 $\mu g/m^3$ are possible when sampling for one hour at 2.0 L/min.

The ThermoSorb/N air sampler contains:

Catalogue Number 6533

Contents

20 ThermoSorb/N air samplers in foil pouches
20 Foil pouch clips
20 Data log work sheets
1 Instruction sheet

Catalogue Number 6525

Contents

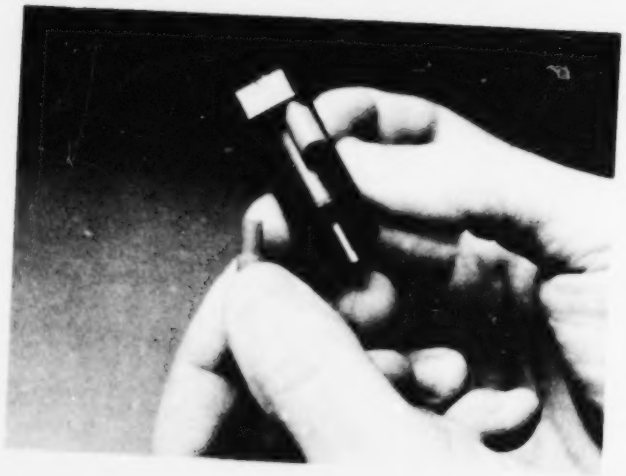
10 ThermoSorb/N air samplers in foil pouches
10 Foil pouch clips
10 Data log work sheets
10 Mailing envelopes for
10 Analyses at the Analytical Services Laboratory of Thermo Electron Corporation
1 Instruction sheet

Other Equipment Needed for Monitoring:

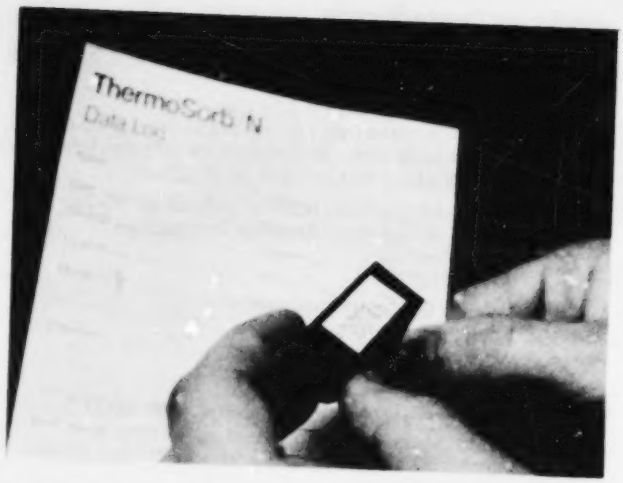
1. Air sampling pump (high flow or low flow)
2. Battery charger
3. Pump calibration — soap bubble tower
4. Tubing, 1/4 in., flexible
5. Stopwatch
6. Scissors

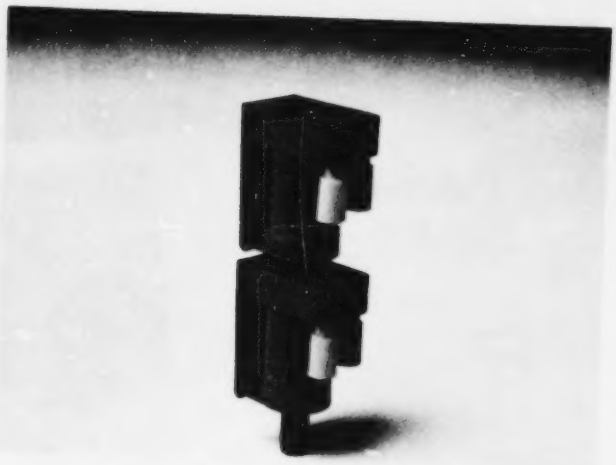
Preparation Before Sampling:

1. Remove the ThermoSorb/N air sampler from the foil pouch. Use scissors to cut open the foil pouch. Save the foil pouch for re-use.



2. Remove the red end caps from the inlet and outlet ports. The red caps can be stored on the ThermoSorb/N air sampler in the brackets under the "AIR IN" sign.





3. Label the ThermoSorb/N air sampler with the peel-off "Air Sampler" label provided on the "Data Log" worksheet. The molded clip of the ThermoSorb/N air sampler provides a flat surface to affix the label.
4. Attach the ThermoSorb/N air sampler to the sampling pump using an appropriate length of 1/4 in. flexible tubing.
5. Calibrate the pump with the ThermoSorb/N air sampler attached. Use a stopwatch and bubble tower to determine the air flow. A 2.0 L/min flow rate is suggested for general monitoring. Flow rates for the ThermoSorb/N air sampler can vary between 0.2 L/min to 4.0 L/min without affecting collection efficiency.
6. Record the air flow and all other appropriate data on the "Data Log" worksheet. The "Data Log" worksheet can be readily applied to a laboratory notebook page.

Sampling:

1. Attach the ThermoSorb/N air sampler

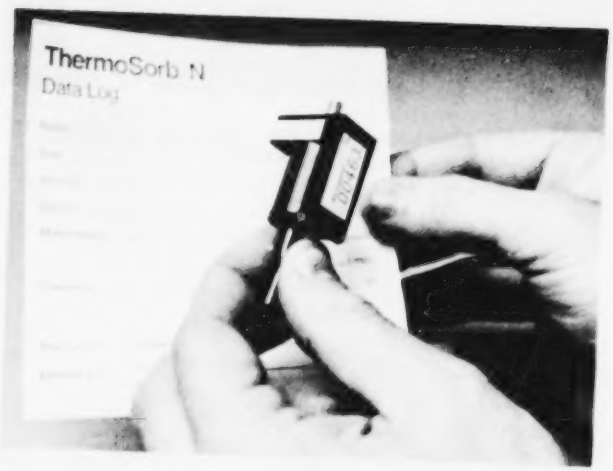
a) In the breathing zone of the worker to be monitored. The molded clip attaches easily to pockets or collars.
b) Near the process to be monitored. The molded clip provides a flat surface so that the ThermoSorb/N air sampler can be easily oriented toward the area of interest.
c) On the pump, in the area to be monitored.

2. Sample for an appropriate period of time. 100L of air total volume is the recommended sample size.
a) For time weighted averages (TWA's) use 0.2 L/min for 8 hrs.
b) For process sampling use 2.0 L/min for 50 min or 4.0 L/min for 25 min.

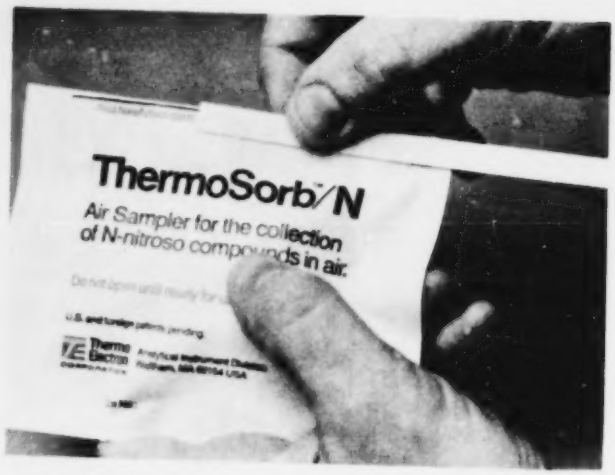
3. If high concentrations of nitrosamines are expected (i.e., over 1500 μg) use another ThermoSorb/N air sampler as a "back-up") section.
4. Note changes in monitoring conditions (the "Air Sampler" label on the "Data Log" worksheet can be used for notes in the field), for example:
a) Obstructions in the ThermoSorb/N air sampler.
b) Changes in flow rate.
c) Changes in ambient temperature, barometric pressure, or relative humidity.
5. Remove the ThermoSorb/N air sampler from the monitoring site.

After Sampling:

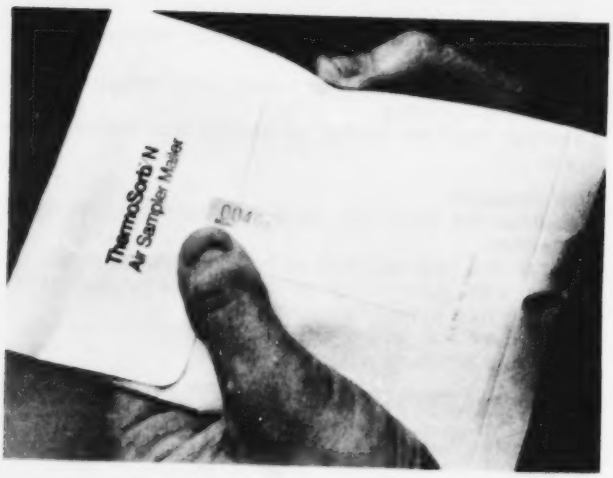
1. Calibrate the pump with the ThermoSorb/N air sampler attached.
2. Detach the ThermoSorb/N air sampler from the pump.
3. Replace the red end caps on the inlet and outlet ports of the ThermoSorb/N air sampler.
4. Record the appropriate data, be sure to include the flow rate after sampling.



5. Affix the "Analysis Vial" label from the "Data Log" worksheet to the ThermoSorb/N air sampler. This can be done on the side of the "AIR IN" sign. The laboratory will then be able to label the analysis vial with a label numbered the same as the ThermoSorb/N air sampler.



6. Replace the ThermoSorb/N air sampler in the foil pouch. Fold the pouch and seal it with the clip provided.
7. Place the sealed foil pouch into a mailer and submit for analysis.



8. Affix the "Mailer Label" from the "Data Log" worksheet as a seal on the back flap of the mailer.

Analysis by Thermo Electron:

1. The Analytical Services Laboratory at Thermo Electron Corporation will report results of analysis within 3 working days after the sample is received.
2. The Laboratory reports results in nanograms.
3. Calculate the concentration of the substance monitored by dividing the results in nanograms by the average volume of air sampled in liters. Results will be in $\mu g/m^3$.

For information on analysis, request publication IS-33, "ThermoSorb/N Air Sampler Analysis Instructions".

For further information:

Call: (617) 890-8700

Write: Thermo Electron Corporation
Analytical Instruments
Waltham, MA 02154 U.S.A.

Telex: 92-3473

Ask for Order Entry, Analytical Instruments, regarding purchase of additional ThermoSorb/N air samplers.

Ask for ThermoSorb/N Customer Service for questions regarding air monitoring.

Ask for Analytical Services Laboratory for questions regarding analysis of the ThermoSorb/N air samplers.

APPENDIX B

Description of the GC-MS System (as Reported to SwRI by NEILS)

Description of the GC-MS System

The GC-MS System consisted of a glass capillary column coupled directly to the ion source of the mass Spectrometer. The column was 20m x 0.25mm i.d. glass, coated with Carbowax 20M. The mass Spectrometer was an AEl MS50 instrument operated at a resolution of 10,000 (10% valley). It was fitted with a peak matching unit and a Daly detector. Hexapole focusing enabled the slits to be fully extended. The accelerating voltage was 8KV and ion current 300μA. The mass Spectrometer was calibrated using a standard solution of N-nitrosodimethylamine (NDMA). 0.3 μℓ sample was injected onto the column via an SGE splitless injection unit. NDMA was detected by monitoring the parent ion (m/e 74.0480) with reference to the fragment m/e 69.9986 of perfluorokerosine. The detection limit of the GC-MS was 1 μg/ℓ of injected material, representing 0.3 pg NDMA.

APPENDIX C

Description of the Nitrosation Capacity Determination (as Reported to SwRI by NEILS)

Description of the Nitrosation Capacity Determination

These samples were collected using an experimental air collector consisting of a ThermoSorb air cartridge filled with a solid sorbent coated with morpholine. These air samples are usually collected using battery driven air pumps with an air flow rate maintained as close to 1 ℓ/min as possible.

In previous experiments in the laboratories of NEILS, 15 of these collectors had been tested in atmospheres containing from 0.5 to 3.0 ppm of equal amounts of NO and NO_2, i.e., 0.25 ppm NO_2 to 1.5 ppm NO_2. Air was drawn through these collectors at 1 ℓ/min for 50 min at 5 different concentrations of NO_x. All tests were run in triplicate. The average amount of N-nitrosomorpholine formed on the three cartridges for each concentration of NO_2 were plotted against the concentration of the square of the NO_2 $[NO_2]^2$. The resulting plot was linear with a slope of 0.81 and had a correlation coefficient of 0.99. The total amount of NMOR formed indicated that 6-8% of the available NO_2 reacted with the morpholine under the test conditions. While the tests were in progress, measurements of the NO_x in the air stream were made at both the entrance and exit of the cartridges. It was observed that the NO levels did not decrease after passage through the cartridge suggesting that this oxide of nitrogen does not contribute to the formation of the resulting NMOR. These cartridges are being developed to aid in determining the comparative amounts of nitrosating agents in industrial atmospheres. However, the nitrosation capacity of airborne oxides of nitrogen have been found to vary with humidity and it is possible that other factors such as ozone may effect the results. While the results from this sampling experiment are only indicative of the absolute amount of NO_2 in the atmosphere, they are useful in determining the qualitative capacity of any given atmosphere to form N-nitrosomorpholine. The methods for analyzing these cartridges are identical to that used for the ThermoSorb/N air cartridges.

As a first approximation, the NO_2 levels that experimentally produce the observed amounts of N-nitrosomorpholine eluted from these air sampling devices are:

$$\text{PPM } NO_2 = \mu g\ NO_2/\ell \times \frac{24.45}{\text{M.W. } NO_2} \times \frac{760}{P} \times \frac{T + 273}{298} \times \frac{1}{0.07^*}$$

$$\mu g\ NO_2/\ell = \frac{\text{M.W. } NO_2}{\text{M.W. NMOR}} \times \frac{\mu g \text{ of formed NMOR}}{\ell \text{ of air sampled}}$$

*Experimentally 6-7% of the NO_2 in the gas stream combines with the surface held morpholine to form N-nitrosomorpholine when the devices have air containing NO_x drawn through them at 1 ℓ/min for 50 min.

Example: μg of NMOR formed on collector = 0.36
ℓ of air sampled = 52

Then $\text{PPM } NO_2 = \frac{46 \times 0.36}{116 \times 52} \times \frac{24.45}{46} \times 1 \times 1 \times \frac{1}{0.07} \simeq 0.021$

APPENDIX D

Description of the Nitrosatable Amine Determinations (as Reported to SwRI by NEILS)

Description of the Nitrosatable Amine Determination

The methods used in this study for sampling and analysis of airborne amines have not been previously described. Amine air samples are collected using ThermoSorb/Amine air cartridges. The methods used to examine the cartridges for amines are similar to those used for the analysis of nitrosamines on ThermoSorb/N air cartridges. Following air sampling, the trapped amines are extracted from the cartridge by back-flushing with methanol with the first 3 mℓ collected for analysis. Aliquots of this eluate are then examined by injecting on a Gas Chromatograph interfaced to a prototype TEA Analyzer operating in the nitrogen mode. The prototype TEA Analyzer (nitrogen mode) used for this study consisted of a Shimadzu Mini 2 GC operating at from 110°C to 180°C, with a flow of 20 cc/min of argon gas through a 1/8" x 12" stainless steel column packed with either 10% Pennwalt 223 on Gas ChromeR or Chromosorb 103 interfaced to a catalytic oxidative pyrolytic furnace. Detection of the NO radical formed from the high temperature oxidation of the amines was by a standard TEA Analyzer. Tests of this sampling and detection method using dimethylamine and morpholine, have demonstrated it to be linear from 0.8 $\mu g/m^3$ to 200 $\mu g/m^3$ with an average recovery of about 90% at all spiking levels. In all respects the detection of amines by this method is similar in linearity and detection limit to that of the standard GC-TEA method for N-nitroso compounds. As a further control, some of the "amine air samples" are examined by a standard Varian GC equipped with an alkaline flame ionization detector (AFID).

APPENDIX E

Task II Trunk and Cargo/Back Seat Sampling Results

APPENDIX E. TASK II TRUNK AND CARGO/BACK SEAT SAMPLING RESULTS

Vehicle	Location[a]	Date	Temp.°F	Nitrosamine Levels, µg/m³	
				NDMA	NMOR
Fairmont	T	11/2/79	45	0.046	ND
Fairmont	T	1/30/81	34	0.027	ND
Fairmont	T	2/17/81	57	0.075[b]	0.038[c]
Fairmont	T	3/18/81	27	0.040	ND
Fairmont	T	4/23/81	64	0.152[d]	0.040[c]
Oldsmobile	B	7/23/79	90	0.470	0.480
Oldsmobile	B	7/31/79	86	0.115	0.511
Oldsmobile	B	6/17/80	75	0.637	3.000
Oldsmobile	B	2/17/81	57	0.058	ND
Oldsmobile	B	3/18/81	27	0.012	ND
Oldsmobile	B	4/27/81	61	0.031[e]	0.044[c]

[a] Location where sample was monitored: T, trunk; B, backseat/cargo area
[b] Confirmed by LC-TEA to be 0.075 µg NDMA/m³
[c] Not detected by LC-TEA
[d] Confirmed by LC-TEA to be 0.140 µg NDMA/m³
[e] Confirmed by LC-TEA to be 0.035 µg NDMA/m³